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EXTRACT FROM PREFACE TO VOLUME 1

IT is in those branches of natural science which border older-established disciplines that the need for critical survey reviews of progress has become greatest. This has arisen partly because subjects such as geochemistry and geophysics fringe and overlap so many other fields and partly because they are at present vigorous growing points in science. A principal aim of the annual series, Physics and Chemistry of the Earth, will be to provide authoritative and up-to-date surveys of progress for those actively engaged in geophysics and geochemistry. But it is hoped also that much of which is written will encourage the interest of the chemist and physicist in a study of our planet, not merely for its own sake, but because such a study often turns out to be of benefit to physics and chemistry. Another aim is to acquaint the geologist with the results and methods of geophysics and geochemistry, particularly as progress in earth science has been hindered by some lack of liaison between different groups.

The subject-matter coming under the heading of Physics and Chemistry of the Earth is vast and only a limited number of topics can be considered in a given volume; in general, an attempt will be made to provide a balanced variety of topics with roughly equal emphasis on chemistry and physics.

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PREFACE TO VOLUME 3

THE theme, origin of the earth, which was started in Vol. 1 has been continued through Vols. 2 and 3. In Vol. 1 SPENCER-JONES wrote a survey on the origin of the solar system from the astronomer's point of view, which was followed in Vol. 2 by an article by UREY on the boundary conditions for theories of the origin of the solar system in which chemical aspects have been emphasized. In Vol. 3 CAMERON's paper on the origin of the elements discusses types of nuclear reactions which may become involved during the formation of the elements. A comparison of the Cameron article with a review published in 1953 by ALPHER and HERMAN (*Ann. Rev. Nuclear Sci.* **2,** p. 1) shows how rapidly this field has developed and changed during the last few years.

These articles on the origin of earth, solar system and elements emphasize the enormous range of scientific disciplines which have to be covered in a study of the physics and chemistry of our planet. They point up also, however, the problem faced by the geophysicist and geochemist when attempting a comprehensive literature survey. In this respect a regular review series such as *Physics and Chemistry of the Earth* should be helpful.

Another general topic, the distribution of the elements, begun in Vol. 1, has been continued through Vols. 2 and 3. So far the halogens and the group III elements gallium, indium and thallium have been surveyed (CORRENS, Vol. 1 and SHAW, Vol. 2, respectively), and in Vol. 3 ADAMS reviews uranium and thorium. The accumulated geochemical data on these two elements is vast, and the review is timely. Among the rest of the articles in Vol. 3, the paper on silicate melt systems by ROEDDER follows more or less naturally on one by ROY and TUTTLE on investigations under hydrothermal conditions in Vol. 1.

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PALÆOCLIMATES

By J. Wyatt Durham

INTRODUCTION

Shortly after it became accepted that fossils (in the modern sense) were the remains of organisms, speculation on climates formerly present in certain areas began. Lyell (1830, pp. 92–143), in the first edition of his classic *Principles of Geology*, devotes three chapters to this general subject. He (*op. cit.* p. 33) likewise notes, for instance, that Robert Hooke (in a posthumous work published in 1705) had concluded "it is necessary to suppose that England once lay under the sea within the torrid zone!"

The occurrence of palms and other types of tropical vegetation in northern latitudes where temperate or frigid climates now hold sway; the finding of elephants and rhinoceroses frozen in the ice of Siberia; and the occurrence of tropical types of shells and corals in Europe: these were the kinds of fossils that caused speculation as to the conditions under which they had lived and that usually led to the conclusion that a tropical or "warmer" climate had existed where they were found.

Much variation has existed in the terms used to denote climates of the past: milder, more benign, more equable, temperate, moderate, tropical, more tropical, warmer, colder, boreal, arctic, glacial and more uniform are qualifying words often used. In rare instances only, until the advent of modern geochemical techniques, has a more precise terminology been attempted. In many cases there has been a deliberate lack of precision, probably because it was felt that the available data did not justify any refinement. At the present time, *tropical* (in a climatic sense) usually indicates average temperatures above 20°C in considering terrestrial climates, but in the sea (Vaughan, 1940, p. 444) *tropical* has been defined as having temperatures above 25°C, and *subtropical* as having minimum temperatures between 15° and 25°C. However Ekman (1953, p. 3) has defined *tropical* as having temperatures above 20°C in the coldest month of the year. At times *tropical* has been considered to include *subtropical*.

Within the marine environment Vaughan (1940) has proposed an additional six zones (three in each hemisphere) based on temperature. These are: two *polar zones*, temperature limits − 1·9° to + 5°C; two *subpolar zones*, temperature limits + 5° to + 10°C; two *temperate zones*, minimum temperatures + 10° to + 15°C. On land the usage of temperature and climatic zones has been more confused with these zones being based on varying definitions and often being confused with "life zones." At times the terms temperate, boreal, arctic, and so forth, have had a purely geographic significance, at other times they have been based on temperatures or other climatic factors. In the *Encyclopædia Britannica* (1952 ed.), under *climate*, the terms *torrid*, *temperate* and *frigid* are applied to the three principal geographic climatic zones, while *tropical* (+ 20°C mean annual temperature), *temperate* (with minimum

temperature 10°C in warmest month), and *cold* (warmest month colder than 10°C) are the three principal temperature zones.

METHODS

In the broad sense palæoclimatology should be concerned with the occurrence in past geological time of all the factors (temperature, precipitation, winds, etc. and their seasonal distribution and variation) considered by the climatologists, but to those concerned with the evidence from the marine record, it has often been limited to palæotemperatures only. The methods used to arrive at these conclusions are many. Most of the interpretations of past years have been based on the palæogeographic distribution of organisms that are either still living or closely related to living taxae of supposed thermophilic (warm-limited) or frigophilic (cold-limited) character, or on supposedly significant associations of organisms. At other times, lithological features of the rocks, such as the occurrence of arkoses, salt deposits, gypsum, redbeds and coal, have been used. In recent years, with the rise of geochemistry, the relative abundance of certain isotopes (such as ^{16}O and ^{18}O), the crystalline form (aragonite–calcite ratio), the presence and relative abundance of certain elements or compounds (magnesium, strontium, amino acids, etc.), and other chemical means have been used, often with a degree of precision seemingly much greater than that obtained by the more long-standing methods. However additional work (LOWENSTAM and EPSTEIN, 1954; LOWENSTAM, 1954; CHAVE, 1954) has shown the need for more data regarding the biological processes involved before the results obtained by chemical means can be properly evaluated.

LOWENSTAM and EPSTEIN (1954, pp. 207–209) have pointed out that many organisms secrete their skeletal material only during a part of the temperature range at a given locality, and that this threshold varies for different organisms. Thus analysis of the shells of the various components of a fossil assemblage may indicate different temperatures at the time of deposition even though they all lived together. After fossilization, various geological processes may modify the chemical composition of the remains of an organism: percolating waters may change the chemical composition; pressure and heat can alter the mineralogical composition. In using isotopic and other chemical analysis, care must be exercised to obtain a fair sample of the original population and to make sure that no significant alteration has occurred subsequent to death or burial.

The utilization of the presence (or absence) of different kinds of organisms for recognition of past climates is founded on "the basic assumption of uniformitarianism—namely, that the animals and plants of the past lived under essentially the same environmental conditions as do their living relatives . . ." (LADD, 1957a, p. 1). Some of the various organisms that have been used in this manner are listed by DURHAM (1950, pp. 1247–1249).

In using "uniformitarianism" in interpreting the presence (or absence) of certain organisms or assemblages of organisms much care must be exercised. KIRK (1928) has drawn attention to many of the false assumptions and hinderances. WOODRING and BRAMLETTE (1950, p. 99) have concluded that the range of living species closely related to, or identical with fossils cannot be used as "a close guide" to reconstruct past environments because the physiological requirement of the organism may have changed. It does not seem probable that the extreme conservatism of Woodring and Bramlette is justified, and even

they were inconsistent in its application. They were impressed by the incongruous association in the fossil record of species whose present day ranges are in some cases separated by hundreds of miles. Perhaps the most common anomaly of this sort occurs with respect to the distribution of "northern" (or supposed "cold water" limited) and "tropical" (or supposed "warm water" limited) organisms. Some of the incongruities are due to "upwelling," a phenomenon whose effects on distribution have only recently been recognized (DAWSON, 1951; EMERSON, 1956b; VALENTINE, 1955). In association with "upwelling" Emerson found "northern" species that were several hundred miles south of their "normal" range. In short distances laterally the faunas consist of typical "southern" species only, so that it is easy to obtain anomalous associations of dead shells. It is a well known fact that shells or remains of dead organisms may be transported considerable distances from their life habitat (LADD, 1957b, pp. 31, 37–40, 49–50, 53).

Other apparent incongruities may be due to inadequate understanding of the factors controlling distribution of "northern" types. The pelecypod genus *Patinopecten* lives along the Pacific Coast of North America only north of San Francisco Bay. In consequence it has often been cited (e.g. SMITH, 1919, pp. 130–131) as indicating a "northern" or cool temperature. However this same genus occurs (DURHAM, 1950, p. 1244) in the Plio-Pleistocene of the Gulf of California in the same beds as, and in close proximity to reef type corals and other tropical elements. It is obvious in this case that the environment was tropical. Other similar cases could be cited.

In general it seems that many more members of cold water faunas are euryopic than members of warm water faunas. Perhaps their euryopic nature indicates that they are less specialized, and therefore less well suited to particular environments in the warmer seas, and in consequence they will invade these areas only if a niche becomes available. When a more efficient occupant of the niche appears, the invader has to retreat to the cooler (and less favourable?) habitats. This general hypothesis seems to be borne out by the much greater diversity of organisms in the tropics as contrasted to the polar regions. MACGINITIE (1955, p. 171) notes that only thirty pelecypods and eighty-nine gastropods were found in the extensive recent studies of the marine fauna of the Point Barrow, Alaska, region. This is in marked contrast to the size of the shelled molluscan fauna of marine tropical areas like the Panamic where the total number of species is estimated to be around 2500. In both areas by far the major portion of the fauna lives in "shallow" water, thus seemingly indicating that warmer temperatures (in contrast to variations in depth, light penetration, and type of substrate) are responsible for the greater diversity of the tropics.

In a study (DURHAM, unpublished) of the distribution of 964 gastropod genera (11,580 records from 2062 localities); twenty-six of 108 genera recorded from the "polar" (below 5°C surface temperature) zones were restricted to that region; 211 of 532 genera were restricted to the temperate (surface temperature range 5° to 20°C) zones; and 384 of 671 genera were restricted to the tropical (surface temperature above 20°C) zone. Only forty-eight genera were found in all three zones, and over half of the tropical genera were restricted to the tropics (as defined by surface oceanic temperatures). On a species level the restriction to the tropical areas is still greater. In this study, some of the genera were represented by only one or two records, and thus their restriction to a zone may not

be significant. Of the genera restricted to the polar zone, in only one case (*Valvatella*) was the restriction supported by more than ten records. Within the tropical zone, however, fourteen genera, with more than twenty-five records each, were restricted, and an additional twenty-one genera with more than twenty-five records were largely restricted. The distribution of the gastropod genera would strongly support the hypothesis that the tropical elements are more significant than cool water elements. If this hypothesis is true, then many interpretations of the presence of "cold water elements" in faunas (e.g. DAVIES, 1934, pp. 69, 76; SMITH, 1919, pp. 131, 145, etc.) are not significant in terms of climate.

As indicated above the presence of thermophilic organisms seems to be much more important than the presence of "cool water" elements, but their significance must be supported by evidence (such as growth stages) that they lived (in the sense of completing a life cycle) where found. It is well known (e.g. SVERDRUP *et al.*, 1942, pp. 862–863) that organisms, particularly planktonic ones, may be carried out of their normal warm water environment and live there for considerable periods but not be able to reproduce. Within the marine environment frigophilic organisms can usually find suitable temperatures in deeper water within the same region, and they are thus not significant in terms of the regional climate. The gastropod *Fusitriton oregonensis*, common in intertidal areas from Puget Sound to Alaska is found only in deeper water off southern California (see WOODRING, 1938, p. 24; WOODRING *et al.*, 1946, p. 72), but characteristic shallow water tropical genera such as *Cypraea* have no such alternative.

LIMITATIONS

Inferences about past climates are based on certain assumptions and limitations. The first and most significant of these assumptions is of course the "Principle of Uniformitarianism," that is that the principles and processes operating in the past are the same as those of today. This is one of the basic tenets of geology and its related sciences.

In the present paper it is also assumed that there has been no "Continental Drift" and/or "Polar Wandering" (at least with respect to the earth's rotational axis). If this assumption is not made, the inferences for particular localities are still valid, but regional or world-wide syntheses of the data cannot be made until the relative geographic positions of the individual localities can be fixed by means of other data. The reasons for making this assumption during the Tertiary have been discussed elsewhere (DURHAM, 1952). In essence, these reasons are:

(1) All known marine faunas of Early Tertiary age in the present tropical belt are of tropical character.
(2) The character of marine Early Tertiary faunas outside of the present tropical belt indicates that at this time the boundaries of the tropics were much farther poleward, but still essentially parallel to those now existing and not compatible with some other position of the rotational pole.

This interpretation, based on the marine faunas is fully supported by the evidence from the Early Tertiary floras of the northern hemisphere (CHANEY, 1940).

In arriving at conclusions about past climates, the distribution, abundance, and

mode of preservation of fossils and sediments of the particular age concerned impose obvious limitations. As yet no means of arriving at an interpretation of climate from igneous rocks has been proposed. If there are no fossils or sediments of a particular age in an area, no direct conclusions can be made about that area at that time. A secondary, but nevertheless important qualification is the magnitude of the time interval under study and the degree of precision with which assignments to the interval can be made. Within the Pleistocene there are numerous instances of climatic changes documented by fossil occurrences, but which as yet cannot be integrated into a coherent scheme because their age relationships are uncertain. The development of carbon isotope dating techniques has helped greatly in the latest Pleistocene, but since this technique at present is not valid for ages greater than about 35,000 years, other similarly precise dating techniques must be (and are) developed for the remaining 950,000 years (more or less) of the epoch.

The extent to which remains of organisms are preserved as fossils in the rocks, and subsequent to that, the extent to which the fossil biotas have been studied control the significance of conclusions based upon them. Nevertheless, even in limited assemblages the presence of stenopic organisms such as reef corals may outweigh limited knowledge of the associated organisms. The modes and possibilities of preservation in the fossil record have been generally discussed by LADD (1957a, pp. 9–25). However as a measure of the adequacy (or inadequacy) of the fossil record it should be pointed out that whereas living tropical shelled molluscan faunas (from all habitats) are estimated to number between 2000 and 2500 species in any one region (e.g. Caribbean or Panamic Regions), fossil molluscan faunas reputedly well studied usually number far fewer species. For example only 352 molluscs are recorded from the upper Eocene Jackson fauna (of tropical character) of the Gulf Coast of the United States (DURHAM, 1952, p. 330). In all fairness however it should be pointed out that the known fauna in this case does not include a deep water facies and rocky coast habitats are largely unrepresented. By far the best known fossil molluscan fauna is that of the Paris Basin Eocene. About 3600 species and varieties have been recorded from the Palæocene and Eocene of this area. This interval probably includes over a third of the 60 million years of the Tertiary and in many lineages much evolution took place. Probably a large percentage of the fauna was replaced several times because of this evolution and the actual known fauna of each moment of time is much smaller. The hazards of burial and fossilization may reduce the apparent size of faunas greatly. Wave action, scouring by currents, the action of scavengers in comminuting hard parts, the hazards of collection, and other less well known factors tend to reduce the apparent size of fossilized biotas.

The quality of the systematics involved in the comparison of faunas needs to be carefully considered. The differences between the systematics of present day "lumpers" and "splitters" may be of the same magnitude as between those of today and those of Linnaeus. Thus faunal lists cannot be directly compared until the level of the systematics has been evaluated.

Conclusions based on physical and chemical analyses are limited: first by the extent to which the materials used for analysis have been modified subsequent to their formation or burial in the rocks, and second by the extent to which the processes controlling their formation are understood.

INTERPRETATIONS OF PAST CLIMATES

During the past twenty years there has been considerable work in the field of palæoclimatology, much of it using the newer techniques. In the "Bibliography and index of geology exclusive of North America" for 1954, thirty-five titles appear under this subject heading. In the "Bibliography of North American geology" for 1952 and 1953 there are thirty-eight titles on the same subject. Of these seventy-three titles, thirty-six are concerned only with the Pleistocene and post-Pleistocene. The results obtained in these various studies are for the major part in general agreement, but a few are markedly at variance with one another. Obviously it is impossible to review all these papers within the limits of the present article, so some of the conclusions dealing with four different aspects and methods have been selected for presentation. These are followed by a general discussion of past climate.

Tertiary Terrestrial Climates of North America

Plants in general seem to be much more sensitive to the different facets of climate than animals, and as a result palæobotany, when there are adequate floras available, gives much detailed information about the different aspects of

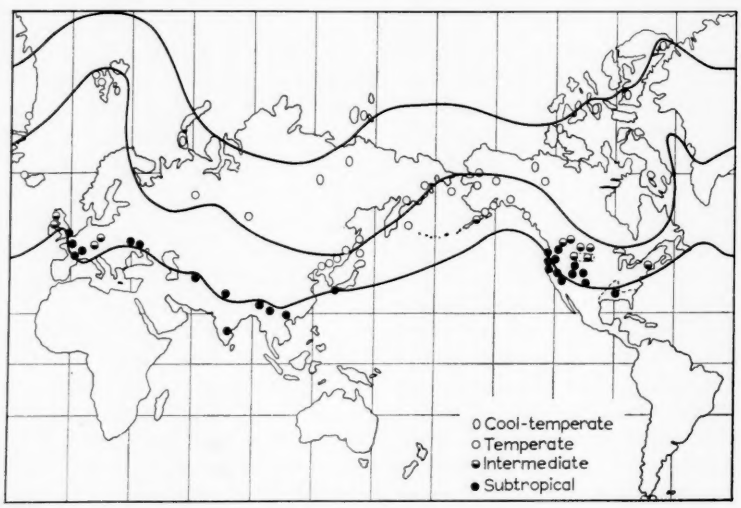

Fig. 1. Distribution of Eocene isoflors in the Northern Hemisphere. (After CHANEY, 1940, Fig. 2.)

past terrestrial climates. Fossil floras of Tertiary age in the northern hemisphere are widespread, in both time and space, and many of them have been well studied. CHANEY (1940) discussed these northern floras in general, and emphasizing those around the rim of the North Pacific, compared them with modern floras and gave his conclusions regarding Tertiary climates. Some of his conclusions have been modified in detail by work such as that of AXELROD (1956), and DORF (1955) but the general results presented are still valid.

CHANEY (*op. cit.*) concluded first of all, on the basis of the floral distribution, that the geographic positions of the continents during all the Tertiary was the

same as that now existing. Second, he showed (*op. cit.* pp. 474–475) that floras of a "subtropical" type extended much further poleward in the northern hemisphere during the early Tertiary than at present (Fig. 1), and that during the later Tertiary they gradually retreated towards the tropics until the present distribution pattern was attained. He likewise concluded that the climatic zones of the early Tertiary had distribution patterns similar to those now existing, but that their boundaries were more poleward. He notes (*op. cit.* p. 484) ". . . in both North America and Eurasia, older Tertiary floral units ranged somewhat farther north on the windward than on the leeward coasts," a distribution pattern essentially like that of today.

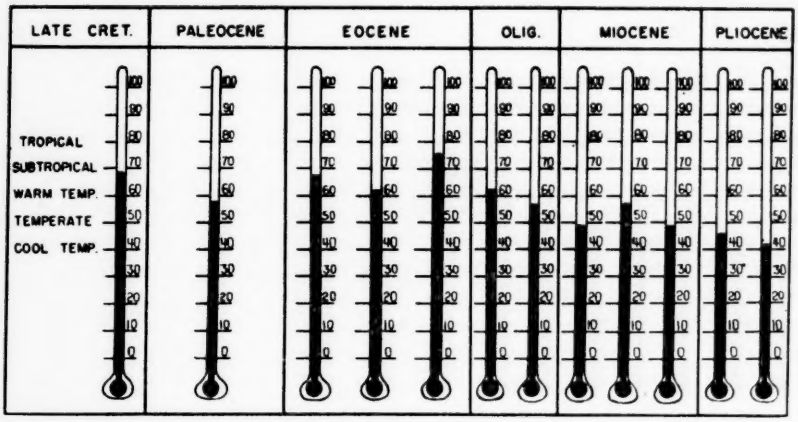

Fig. 2. "Thermometers of the Ages." Generalized climatic regime of Late Cretaceous and Tertiary in middle latitudes (Lat. 40° to 50°N) of western United States. Figures indicate approximate mean annual temperatures. (After DORF, 1955, p. 587, Fig. 3.)

The evidence presented by Chaney also indicates, for instance, that lowlands extended eastward across California, Washington and Oregon until near the end of the Miocene—until that time there were no Cascade Mountains or Sierra Nevada-Coast Ranges to separate a humid coastal belt from an interior arid one.

Chaney did not define his terms "subtropical," "temperate," etc. but DORF (1955, p. 587, Fig. 3) in considering the same part of the western United States concluded that the mean annual temperatures at latitudes between 40° and 50°N, varied (Fig. 2) from a maximum of about 23·9°C in the upper Eocene to about 5·5°C in the late Pliocene. DORF (*op. cit.* pp. 588–589) also points out that Tertiary climates in the southeastern United States and northwestern Europe followed the same trends as in western United States. COLBERT (in SHAPLEY *et al.*, 1953, pp. 266–269) concludes that the terrestrial vertebrates show the same climatic trends as plants during the Tertiary.

Tertiary Marine Climates

The writer (DURHAM, 1950, 1952) has discussed the Tertiary marine climates of the Pacific Coast of the United States and the Eocene marine climates of the world. Such additional evidence as has become available since then has caused only minor changes in the conclusions presented in those two papers. "Climate"

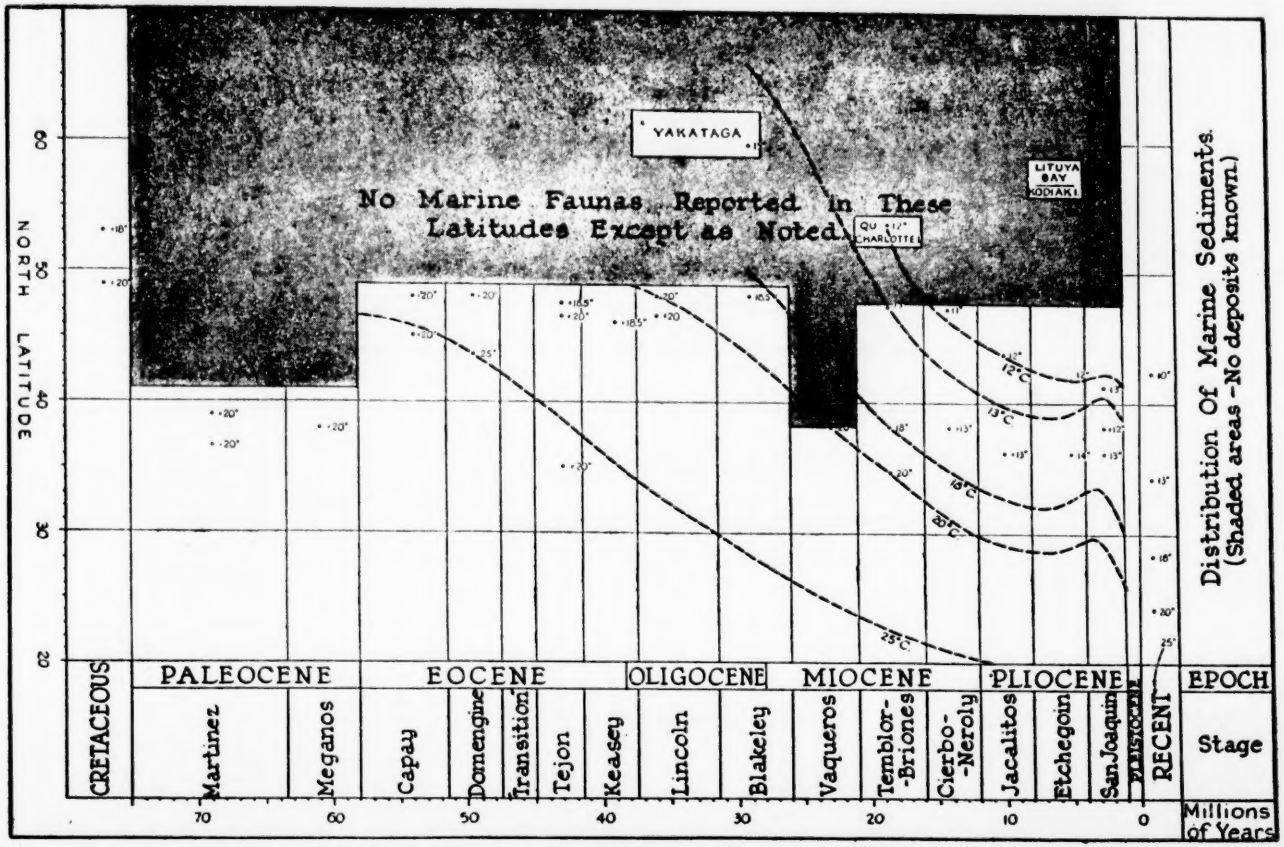

Fig. 3. Past positions of February marine isotherms along the Pacific Coast. (After DURHAM, 1950, p. 1259, Fig. 3.)

as used in those papers was largely restricted to temperature, although of necessity inferences as to depth of deposition (corresponding to elevation in terrestrial environment) were also made. Thermal conclusions were made in terms of average water temperatures prevailing at the surface of the oceans during the coldest month of the year (February in the northern hemisphere).

It was concluded first of all (DURHAM, 1950, pp. 1244–1247; 1952) that the evidence from the early Tertiary marine faunas militates against any shifting of the continents ("continental drift") since the Mesozoic, and as a corollary to this, that the north pole had also occupied the same position as at present. Secondly, on the Pacific Coast (DURHAM, 1950, pp. 1251–1260) the tropical zone on the oceans extended north of 50°N latitude in the Eocene (Fig. 3) and gradually retreated southward during the Tertiary, with recognizable oscillations in the late Pliocene and Pleistocene. This climatic pattern is in accord with that presented by CHANEY (1940) for the terrestrial climate of the same region. Thirdly, it was shown (DURHAM, 1952, pp. 332–339) that the same poleward extension of the tropical zone (Fig. 4) occurred on a world-wide basis during the Early Tertiary. When faunal lists of the later Tertiary are examined on a world-wide basis and using the same criteria, a gradual retreat, in time, of the isotherms towards the Equator, as on the Pacific Coast, is apparent. Again these conclusions are in accord with those of CHANEY (1940), COLBERT (in SHAPLEY *et al.*, 1953), and DORF (1955) for the terrestrial climates.

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Upper Cretaceous Marine Temperatures Based on Oxygen Isotopes

The recognition of a temperature factor in control of the $^{18}O/^{16}O$ depositional ratio of calcium carbonate prompted a series of determinations of palæotemperatures by means of this ratio. LOWENSTAM and EPSTEIN (1954) summed up the results of their investigations to that date. The usefulness of this method depends upon the unaltered condition of fossilized shells and they found that among the common Cretaceous fossils, belemnite guards were usually not altered and thus the most useful. They also found that in general the shells of other invertebrates, such as brachiopods, Ostreidæ, and *Inoceramus*, recorded a higher temperature than the associated belemnites. This is in accord with their investigation into the deposition of carbonate in the shells of living organisms in Bermuda where they found that different species had characteristic temperature ranges in which the shell was deposited and that most species did not record the total temperature range of their environment.

LOWENSTAM and EPSTEIN (*op. cit.* p. 247) caution that the ". . . study is solely an exploratory investigation of the potential application of the paleotemperature method, and hence the interpretations must be regarded as probable rather than definite." Their general findings on the basis of belemnites and brachiopods for the Upper Cretaceous of western Europe show (Fig. 5) a high in late Albian, a low (about 16°C on basis of belemnites) in the Cenomanian followed by a gradual increase until the Coniacian-Santonian (about 20°C on basis of belemnites), followed by a decline (to nearly 16°C) in the lower Maestrichtian, and finally a rise again in the later Maestrichtian. Whatever the significance of these mean temperatures in terms of the life habitat of the belemnites (the brachiopods consistently indicate higher temperatures), it is worthy of note that these temperatures are between 6° and 10°C higher than the mean annual temperatures of the adjacent seas at the present time and that they indicate

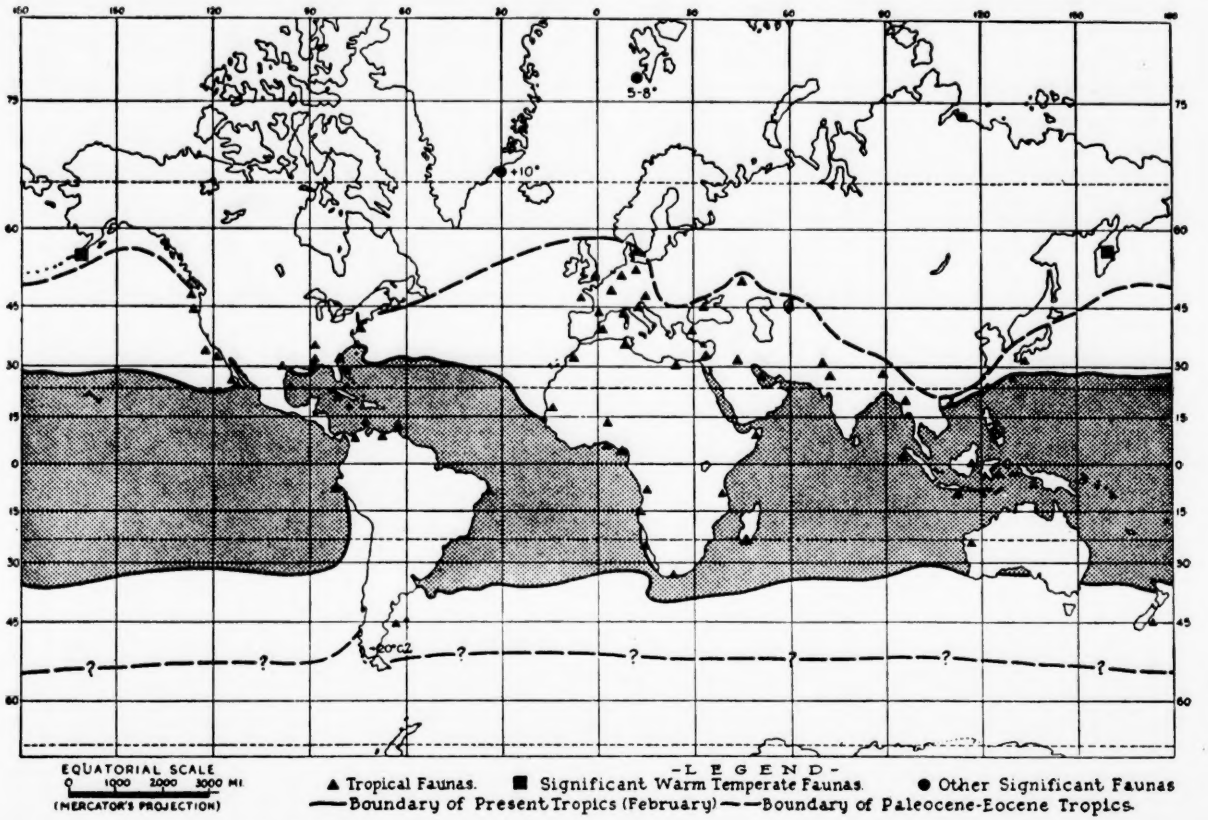

Fig. 4. Paleocene–Eocene tropical zone. (After DURHAM, 1952, p. 338, Fig. 1.)

subtropical to tropical surface marine temperatures for western Europe during the Upper Cretaceous. This poleward extension of the tropical zone is in accord with the conclusions of DURHAM (1950, p. 1252) and DORF (1955, pp. 587–588) for the Cretaceous of the Pacific Coast of North America from different lines of evidence, and of COLBERT (in SHAPLEY *et al.*, 1953, pp. 264–266) for the Cretaceous as whole from the evidence of fossil vertebrates.

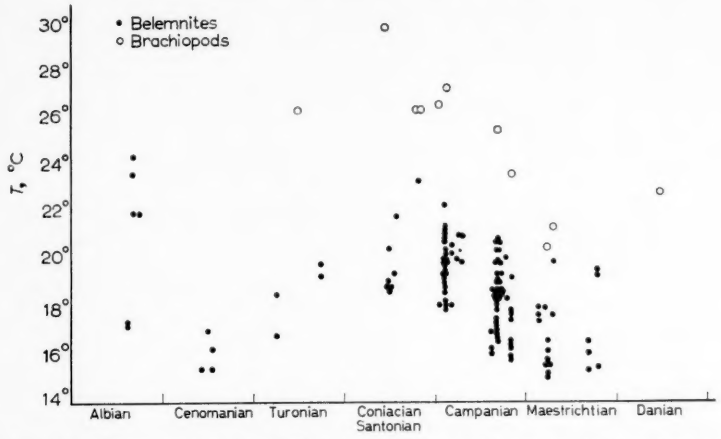

Fig. 5. Mean-temperature distribution of belemnites and brachiopods from Albian to Danian in western Europe. (After LOWENSTAM and EPSTEIN, 1954, p. 226, Fig. 10.)

As in the Early Tertiary, the evidence from several different lines of reasoning points to much more widespread tropical climatic zones than at present. The detailed evidence from oxygen isotope analyses suggest that there were expansions and contractions in the geographic expanse of the tropical zone.

Pleistocene Oceanic Temperatures

As noted earlier the difficulties attendant upon making refined correlations of small time intervals in the Pleistocene has hindered a synthesis of much available climatic data. However the recent development of long coring devices has made long cores, in many instances apparently representing continuous sedimentation, of oceanic sediments available. Some cores of this type have been interpreted as containing a complete representation of the Pleistocene (ARRHENIUS, 1952, p. 192, Fig. 3. 3. 1; EMILIANI, 1955, p. 547). Various methods and combinations of methods (see ARRHENIUS, 1952; EMILIANI, 1955, 1957; and ERICSON *et al.*, 1956), including oxygen isotope ratios, carbonate ratios, distribution of thermophilic species of foraminifera, radiocarbon dating, titanium content as a function of age, percentage of biogenous silica, amount of nitrogen and amount of phosphorus are being used to arrive at a detailed history of the marine Pleistocene.

Nine warm stages alternating with nine cold stages were recognized in the eastern Pacific by ARRHENIUS (1952, pp. 18, 199) in the interval he assigned to the Pleistocene. Arrhenius summarized his results in a graph (Fig. 6) expressing rate of atmospheric circulation, with maximum circulation corresponding to

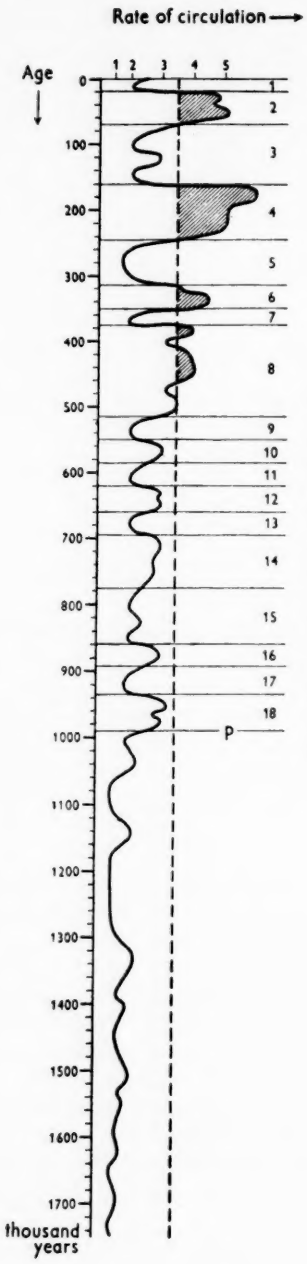

Fig. 6. Rate of low latitude atmospheric circulation as a function of time. The abscissa scale is arbitrary and the relative amplitudes of the circulation changes are inferred mainly from the quantitatively measured rate of accumulation of calcium carbonate, the qualitatively estimated rate of dissolution of calcium carbonate and the quantitatively determined microfossil distribution. The dashed line corresponds to the inferred minimum rate of circulation occurring in connexion with extensive glaciations. The Pleistocene main stages (1–18) are indicated and their approximate boundaries drawn in the diagram. P is the climatic Pliocene–Pleistocene boundary. (After ARRHENIUS, 1952, p. 199, Fig. 3. 4. 2.)

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periods of extensive glaciation, and minimum circulation to warm interglacial periods. Thus instead of the usual four or five major cold intervals commonly recognized in the Pleistocene, Arrhenius' data would indicate nine. EMILIANI (1955) in summarizing the data from deep-sea cores has apparently accepted Arrhenius' interpretations from the Pacific, and integrating them with other work from the Atlantic, has correlated the results with the standard American and European glacial chronologies (Fig. 7). The general results indicate that

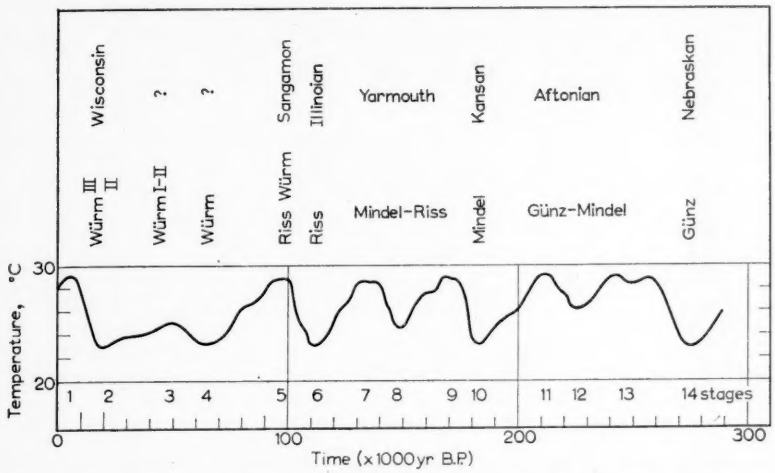

Fig. 7. Generalized low latitude oceanic temperature variations correlated with terrestrial glaciations for part of Pleistocene. (After EMILIANI, 1955, p. 569, Fig. 15.)

mean annual surface oceanic temperatures in the low latitudes fluctuated by about 6°C during the Pleistocene.

The results arrived at by ARRHENIUS, EMILIANI, and ERICSON *et al.*, are in strong contrast to those of CRICKMAY (1929) who recognized seven climatic zones in a lower Pleistocene near shore marine section near Los Angeles, California, slightly under seventy-five feet thick. His interpretations were based on fossil associations, with the incongruities ascribed to the presence of derived fossils. Most workers in the same area do not at present accept his conclusions.

Past Climates—Generalities

If the conclusions presented above for Cretaceous and later climates are valid —and there seems no escaping their general validity if the principle of uniformitarianism is accepted—one conclusion seems inescapable. This is that the present restriction of tropical climates to a relatively narrow belt (and in periods of glaciation to an even narrower belt) of the earth's surface is an unusual situation (Fig. 8). The evidence for the Cretaceous and Tertiary indicates that for most of the time prior to the Pliocene the tropical zone was more widespread than now, and that during certain intervals at least, the boundary of the tropics was at some point between 50° and 60°N latitude in the northern hemisphere and occupied a similar position in the southern hemisphere. The evidence becomes more difficult to interpret in pre-Cretaceous times because there are

no close living relatives for most organisms and the fossils are more often poorly preserved or are chemically altered. Nevertheless the conclusions of various workers, such as BARGHOORN (in SHAPLEY *et al.*, 1953, pp. 239–243) on the palæobotanical evidence, COLBERT (in SHAPLEY *et al.*, 1953, pp. 249–264) on the evidence from fossil vertebrates, LOCHMAN (1957, pp. 154–157) on the Cambrian and Lower Ordovician of Montana, CLOUD and BARNES (1957,

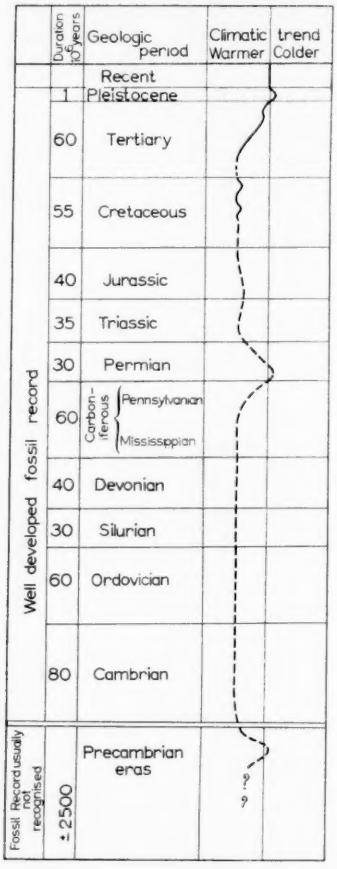

Fig. 8. Generalized climatic trends in middle latitudes.

pp. 195–196) on the Early Ordovician of Texas, BROOKS (1949, pp. 21–27, 382) in his discussion of "Climate through the ages" and SCHWARZBACH (1950, p. 160) in his summary of past climates in central Europe, indicate that a more widespread tropical or "warm" climate prevailed over much of the Palæozoic, Mesozoic and Tertiary. Major episodes of glaciation prior to the Pleistocene are also recognized, indicating that there have been major fluctuations in world-wide climate.

TING YING H. MA in his detailed studies on corals (1937a, b) has presented much valuable information showing how variations in temperature affect the

growth of corals, and how this variation may be recognized in fossils. Ma has also published several thick volumes (especially his series *Research on Past Climate and Continental Drift*) attempting to synthesize his data but his compilations reflect his lack of access to the world-wide literature.

There seems to be no general agreement as to the causes of climatic variation. Alternating intervals of high and low topographic relief of the earth's surface, variation in heat due to internal radioactivity of the earth, changes in the composition of the atmosphere, variation in radiation from the sun, astronomical and cosmical changes, presence of large amounts of volcanic dust in the earth's atmosphere and variations in circulation patterns are some of the causes that have been evoked to explain the changes.

In summary it seems highly probable that as our techniques are refined and as new methods are developed that our knowledge of the climates of older geological intervals will be much increased in detail and precision.

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GEOPHYSICAL INVESTIGATIONS IN THE EASTERN CARIBBEAN: SUMMARY OF 1955 AND 1956 CRUISES

By C. B. Officer, J. I. Ewing, J. F. Hennion, D. G. Harkrider and D. E. Miller

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INTRODUCTION AND ACKNOWLEDGEMENTS

During the past several years there has been a number of investigations of crustal structure beneath oceanic areas through the use of seismic refraction techniques. These investigations have led to an increased knowledge of the composition and structure of the geologic strata and crust underlying such areas as the ocean basins themselves, oceanic islands and their immediate vicinity, mid-ocean mountain ranges, continental margins, basins of interior seas, and island arcs and deep sea trenches. This paper is concerned with an intensive examination of an island arc and deep sea trench and its associated interior basin.

The area covered is shown in Fig. 1 and 2. Briefly the geography is as follows. To the east and north-east is the Atlantic basin. To the west is the interior Venezuelan basin. The depths of water in the Venezuelan basin, around 2500 fathoms, are nearly as great as those in the Atlantic basin. Between the two are the Lesser and Greater Antilles island arc, the Puerto Rico trench, and the Barbados ridge. The island arc of the Lesser Antilles extends out from South America and curves around to the north-west. It is continued to the west by the Greater Antilles of which the island of Puerto Rico and the eastern tip of Hispaniola are shown in Figs. 1 and 2.* Exterior to the island arc is the Barbados ridge. It is a continuation of the Venezuelan geosyncline of north-eastern Venezuela and Trinidad. It also curves around to the north-west and gradually disappears as a topographic feature north-east of the island of Guadalupe. Its axis lies between that of the Antilles island arc and the Puerto Rico trench. The Puerto Rico trench parallels the island arc. It is deepest north of Puerto Rico and curves around to the south-east at diminishing depth. These are the major geographic features. Of smaller size is the Aves swell, a broad swell interior to the island arc. The area between the Aves swell and the Lesser Antilles is referred to as the Grenada trough. The area between the Lesser Antilles and the Barbados ridge is referred to as the Tobago trough.

The locations of the seismic refraction profiles have been shown on Fig. 1. The first set was made during the spring of 1955 and the second during the summer of 1956. The 1955 work was conducted from the research vessels *Atlantis* and *Caryn* and the 1956 work from the research vessels *Atlantis* and

* The bathymetry for Figs. 1 and 2 came primarily from U.S. Navy Hydrographic Office chart 5487.

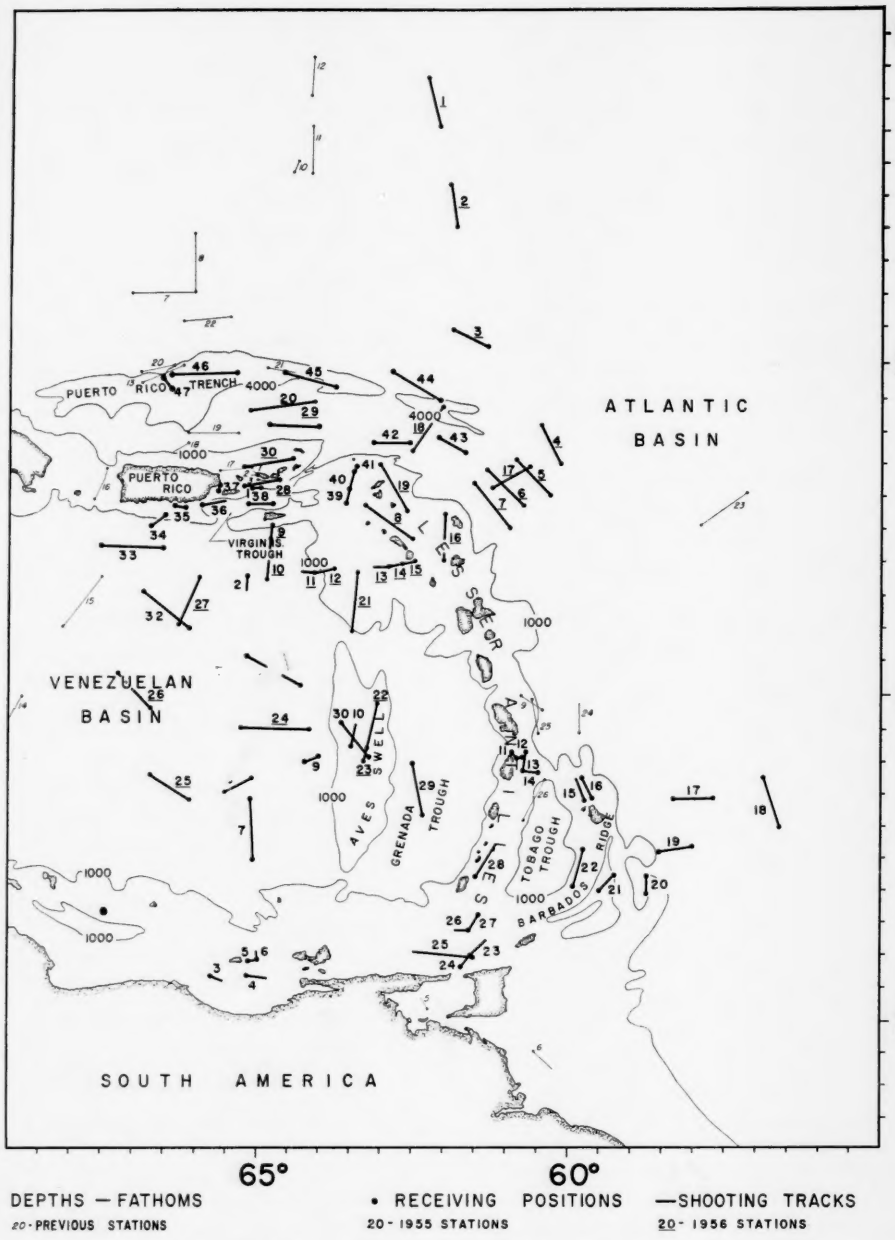

Fig. 1. Geographic map of Eastern Caribbean with seismic refraction stations.

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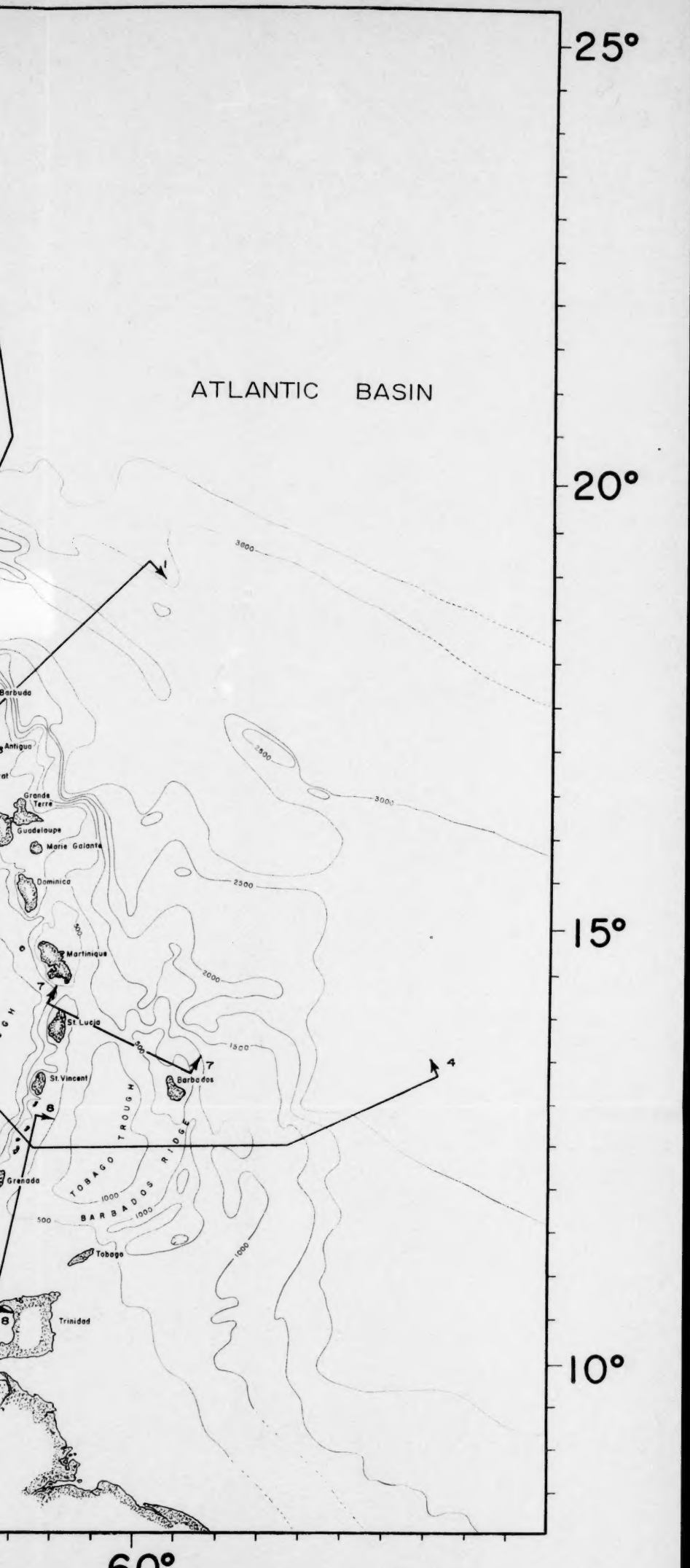
Fig. 2. Geographic and bathymetric map of East



f Eastern Caribbean with cross-section lines.

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Bear, all of the Woods Hole Oceanographic Institution. A great deal of the success of both cruises was due to the fine co-operation of captains W. S. Bray, E. J. Mysona and A. Karlson and the crews of the *Atlantis*, *Bear*, and *Caryn* respectively. The scientific equipment for both cruises came from the Woods Hole Oceanographic Institution and the Lamont Geological Observatory, Columbia University. The scientific personnel engaged in one or more phases of the 1955 cruise were A. Bradshaw, W. Dunkle, G. Duys, R. S. Edwards, J. Hahn, H. R. Johnson, W. Moss, C. B. Officer, D. Owen, F. Richards, M. Rutstein, J. Ryther and R. Vaccaro, Woods Hole Oceanographic Institution; J. I. Ewing, Lamont Geological Observatory; W. Hudson, Western Electric Co.; and S. Wardani, Scripps Institute of Oceanography. The scientific personnel engaged in the 1956 cruise were J. I. Ewing and J. F. Hennion, Lamont Geological Observatory; R. S. Edwards, Woods Hole Oceanographic Institution; C. B. Officer, Rice Institute; J. W. Berg, University of Utah; J. Rose, University of Wisconsin; and W. L. Clarke, D. A. Fahlquist, G. Fermi, T. Gifft, D. Lum, and R. P. von Herzen, and L. J. Barnes, D. G. Harkrider, T. W. Lawhorn, M. Loughridge, D. E. Miller and J. J. Sisler, students at Harvard University, Massachusetts Institute of Technology, Princeton University, Cornell University, University of Utah, Scripps Institute of Oceanography, and Rice Institute respectively. These investigations were supported through contracts Nonr 1367, Nonr 2116, Nonr 2129, NObsr 43270, NObsr 43355, and NObsr 64547 with the U.S. Navy and through the Associates Fund of the Woods Hole Oceanographic Institution. The explosives were supplied by the Bureau of Ordnance, U.S. Navy. Drs. J. B. Hersey and C. O. D. Iselin of the Woods Hole Oceanographic Institution and Prof. M. Ewing of Lamont Geological Observatory were helpful in making these expeditions possible. One or more of the five authors of this paper analysed each profile; the conclusions are those primarily of the first three authors. Two papers have been published previously on the results of the 1955 cruise, OFFICER *et al.* (1957) and EWING *et al.* (1957).

A number of other seismic refraction profiles have been made throughout this area. Their locations have been included for reference in Fig. 1. Previous to this investigation there were three profiles around the island of St. Thomas (1–3), one near Barbados (4), and two near the Orinoco delta (5–6) by WORZEL and EWING (1948). HERSEY *et al.* (1952) have two profiles north of the Puerto Rico trench (7–8). TOLSTOY *et al.* (1953) have one profile near Martinique (9) and one profile north of the Puerto Rico trench (10). EWING *et al.* (1954) have two profiles north of the Puerto Rico trench (11–12). HERSEY (unpublished) has one profile in the Puerto Rico trench (13) and SUTTON and M. EWING (unpublished) have nine profiles across the Venezuelan basin and in the Puerto Rico trench (14–22); the results of these profiles have been reported in EWING and WORZEL (1954) and EWING and HEEZEN (1955). J. I. Ewing has four profiles east of the Lesser Antilles (23–26); the results of these profiles have been reported in EWING *et al.* (1957). In addition there are about seventy profiles now being prepared for publication at Lamont Geological Observatory by M. Ewing, J. L. Worzel, J. Nafe, J. Ewing, G. Sutton, J. F. Hennion, J. Antoine, and W. Ludwig. These consist primarily of a line of stations from Trinidad to Curaçao to Cuba, a line from Hispaniola to Panama, a line from the Columbia basin to the Yucatan basin, a line in the Cayman trough, and a line from Cuba eastward into the Puerto Rico trench.

INSTRUMENTATION AND FIELD TECHNIQUES

The instrumentation for these cruises was much the same as that for other marine seismic refraction cruises with some small changes and improvements. For brevity, only the instrumentation on the *Bear* will be described here. It allowed simultaneous recording of information for seismic reflection and underwater sound transmission studies as well as the primary seismic refraction information. On both cruises both ships were equipped to record and to shoot.

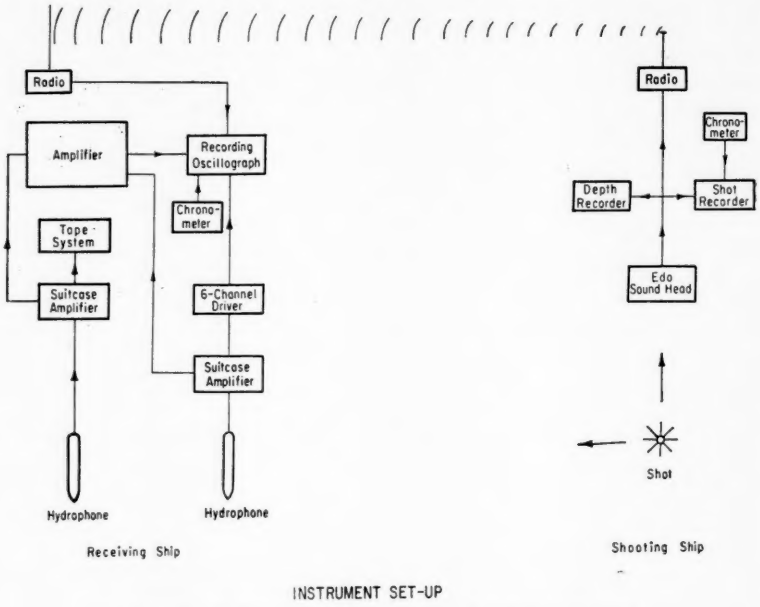

Fig. 3. Block diagram of receiving and shooting equipment.

A block diagram of the receiving equipment is shown in Fig. 3. The detectors were Brush Development Co. type AX58 hydrophones. These hydrophones utilize two Rochelle salt piezoelectric crystals which are immersed in castor oil to give proper acoustic impedance matching to the ocean. The crystal terminals were connected to a cathode follower preamplifier in the hydrophone case to present a low impedance to the hydrophone cable. The receiving amplifier was an accurately calibrated, wide band, large dynamic range amplifier, referred to as a "suitcase" amplifier in Fig. 3. Each "suitcase" amplifier consisted of two separate amplifier channels. The output from one channel of each amplifier went to a Houston Technical Laboratories 7000-B amplifier system, consisting of twenty-four amplifiers with interstage filtering, twelve for each hydrophone. Various band pass filters from 5 to 500 c/s and various dynamic ranges were used on these amplifiers. These outputs then went to a Houston Technical Laboratories recording oscillograph, consisting of twenty-eight galvanometers whose movements were recorded by reflected light on a moving photograph paper. The output from the second channel of one amplifier went to a dual

channel Magnecorder magnetic tape recorder, recording two dynamic levels. No filtering was used. This information was primarily for later seismic reflection and underwater sound transmission analyses. The primary seismic refraction information was contained on the oscillograph records. The output from the second channel of the second amplifier went to a six channel amplifier. Each channel in this amplifier had various interstage filters from 1000 to 10,000 c/s. The resulting signals were rectified and went to the recording oscillograph. These channels were used for the proper recording and identification of the direct sound wave, propagated in the surface isothermal sound channel. This arrival is used for range determination. The various channels of the Houston Technical Laboratories amplifiers were used for proper recording of the refraction arrivals from the strata underlying the ocean floor. In addition to the above the signal from a break circuit chronometer and the signal of the instant of detonation (transmitted by radio from the shooting ship) were recorded on the oscillograph record through separate galvanometers.

A block diagram of the shooting equipment is also shown in Fig. 3. The instant of shot detonation was detected by the echo sounder receiving system, consisting of an Edo Corp. transducer and amplifier. This signal was simultaneously transmitted by radio to the receiving ship and recorded on the shooting ship on a single channel Sanborn Co. direct writing oscillograph. The signal from a break circuit chronometer was superimposed on this latter record.

For receiving operation various techniques have been developed to provide quiet listening conditions. Generally the refraction arrivals were low amplitude, low frequency (5–40 c/s) signals; and it was necessary to have the hydrophone noise level down to the ambient noise level of the ocean for clear recording of these signals. For this purpose all the ship's engines and other machinery were off during the reception of refraction arrivals. Electrical energy was supplied by the ship's batteries. Occasionally other ship noises such as that caused by ballast shifting during the ship's roll or rudder movements would cause noise in the frequency range of interest and would require special precautionary measures. Other objectionable noise may be caused by improper suspension of the hydrophone in the water. If the hydrophone were lowered directly on its cable, the variation in the tension on the cable during the roll of the ship would be transmitted directly to the hydrophone and cause excessive noise. If a surface float were placed along the cable with a long bight to the ship, no noise would be caused by the roll of the ship; but surface wave motion would be transmitted directly to the hydrophone and cause excessive noise. The technique which has been used successfully almost since the first deep water refraction profile by the Lamont Geological Observatory and Woods Hole Oceanographic Institution groups and is, as with many marine geophysical techniques, due primarily to M. Ewing consists of the following. Five or six floats are placed along the hydrophone cable at increasing distances from 10 to 60 ft out from the hydrophone so that with about 200–300 ft of cable out the system has a slight positive buoyancy. Before the expected reception of the refraction arrival sufficient cable is paid out so that the system has a slight negative buoyancy. If arranged properly, the hydrophone sinks at a slow rate of about 20 ft/min. During the reception of the refraction arrival the system is then at depth and free from surface motion. This technique does indeed reach the ambient noise background of the ocean in the frequency range of interest. A period of about 1–2 min of

ambient level can be obtained, sufficient for reception of the information of interest. The importance of this technique cannot be overstated; it is the most important single factor in the success of a long range seismic refraction profile in deep water. Two separate hydrophones were always used to increase the chances of clear reception of the refraction arrivals. In water depths shallower than about twenty fathoms the receiving ship was anchored, and the hydrophones were lowered to the bottom without floats.

The shooting schedule and charge sizes were determined by the receiving ship. The charge sizes varied from $\frac{1}{2}$ to 300 lb of TNT. All charges were detonated by a blasting cap from a length of safety fuse, and all charges were detonated at a sufficient depth so that their gas bubble did not break the surface with consequent loss of low frequency energy to the atmosphere. The instant of detonation was received on the echo sounder transducer and transmitted by radio to the receiving ship for the zero time on its oscillograph record. In addition the shooting ship made a recording of the instant of detonation and the first reflection from the bottom on a direct writing recorder. In case the receiving ship missed recording the instant of detonation but did record the radio transmission of the first bottom reflection, the zero time could be recovered from the shooting ship's record. In case the receiving ship missed or did not receive either the instant of detonation or the first bottom reflection, the zero time could be recovered from the shooting ship's record and the relative rate of the shooting and receiving ships' chronometers determined from other shots in which both had a recording of the instant of detonation. These precautions were important, for it goes without saying that a refraction seismogram without a zero time is of little value.

In addition to the above the shooting ship kept a record of the charge size detonated, the absolute time of the instant of detonation, and the length of time that the charge was in the water before detonation. Further the shooting ship made a continuous recording of the water depth with an Edo Corp. echo sounder and a Woods Hole Oceanographic Institution precision depth recorder, designed by KNOTT and HERSEY (1956). The receiving ship also made an echo sounder record, between shots, of the bottom over which it was drifting. The depths of the receiving hydrophones were determined from a separate depth (pressure) sensing element on the hydrophones. Both ships made frequent bathythermograph lowerings to provide a record of ocean temperature vs. depth from the ocean surface down to a depth of 900 ft; this information is used to compute the velocity of propagation of the direct water wave.

A typical long range, reversed refraction profile of 40 nautical miles or greater took the better part of one day to complete. At the beginning of a profile one ship was hove to for receiving while the second ship then proceeded away from the first on a prescribed course firing shots scheduled by the receiving ship. Each refraction seismogram was developed and read immediately following its reception on the receiving ship, and a running travel time plot was kept of the refraction events from these recordings. Changes in charge size and shooting schedule were made as dictated by these records and the travel time plot. The end of the shooting run was also determined by the receiving ship, generally from the results of its travel time plot. At this point the shooting ship stopped and prepared to receive. The first ship then got under way on the same course as that followed by the second ship and fired shots to reverse the profile. Generally

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the drift of the two ships was nearly the same so that the course followed by the second ship was a true course for the first ship. Occasionally the drift of the two ships while receiving would be different, and a correction in the shooting track would be necessary during the shooting of the reverse profile. The distance between the two ships for any shot was determined from the travel time of the direct sound through the surface sound channel from the shot to the receiving ship's hydrophones. The absolute position of the profile was obtained from the ship's navigation as determined by the ship's officers through celestial fixes and lines of position, sights on islands where possible, and Loran fixes or lines of position where possible. The profile locations shown in Fig. 1 are the average from the two ships' tracks; this average track is generally valid within 2–3 miles. The drift of each ship while receiving was generally between 2–5 miles.

REFRACTION EQUATIONS, RAY PATHS, AND REDUCTION OF DATA

Several seismic arrivals are detected by the hydrophones. These may be divided conveniently into three groups as illustrated in Fig. 4, namely the direct wave (*D*), the bottom and sub-bottom reflections (*Bn*), and the refraction arrivals (*G*). The direct wave is propagated in the surface isothermal sound channel. Throughout this cruise, as is often the case, there is a mixed water layer of constant temperature and salinity down to a depth of 50–100 ft. The sound velocity in this isothermal layer increases slightly with depth (pressure) forming a sound channel with the ocean surface. A portion of the energy from the shot is trapped in this sound channel and propagates directly to the receiving hydrophone. As might be expected the sound channel propagation is frequently dependent; generally frequencies above about 1000 c/s are propagated well. The travel time of *D* multiplied by the sound velocity in the surface sound channel gives the range between the shot and the receiving hydrophone. This is an accurate range determination, valid to within 5 ft in 1 nautical mile. It is the method of range determination for the abscissa of the refraction travel time plots. The sound velocity in the surface channel is dependent primarily on temperature; it is determined from the bathythermograms and experimental tables of sound velocity in the ocean (MATTHEWS, 1939). The bottom reflection arrivals (*Bn*) have followed those ray paths which involve one or more reflections from the ocean bottom. Their frequency spectrum is broad, and generally they are the largest amplitude arrivals. These arrivals are not of primary concern to us here and will not be discussed further. At times the bottom reflection is followed immediately by sub-bottom reflections from horizons as deep as 3000 ft beneath the ocean floor. The refraction arrivals (*G*) enter the higher velocity refracting layer at the critical angle and are propagated parallel to the boundary, reradiating back into the upper medium at the critical angle. There will be a refraction arrival for each higher velocity layer. A refraction arrival is not detected at the receiving hydrophone until the range corresponding to the offset distance of its critical angle ray has been passed. The refraction arrival from a given layer will always arrive sooner than the corresponding reflection from the top of that layer. The refraction arrivals generally have small amplitudes and low frequencies (5–40 c/s). From Fig. 4 it should be clear that the travel time plots of the bottom reflections for a constant velocity ocean and a horizontal bottom are hyperbolæ. It should also be clear that the travel time plots of

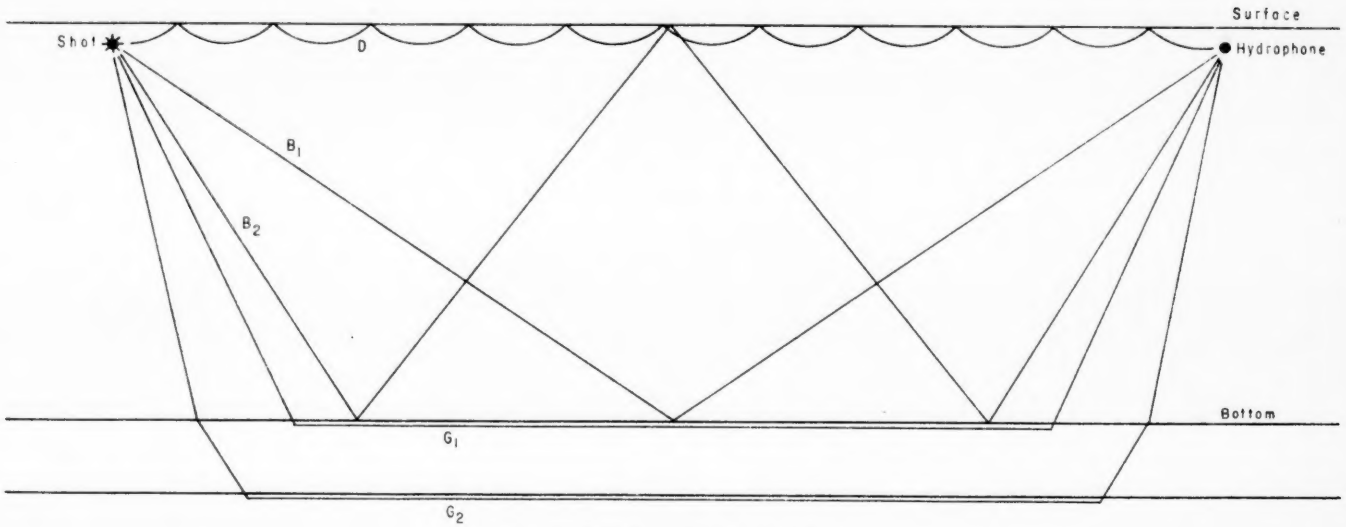

Fig. 4. Ray diagram of *D*, *B* and *G*.

the refraction arrivals for planar refracting surfaces are straight lines. For a more comprehensive discussion of these various points reference may be made to OFFICER (1958).

An abbreviated derivation taken from EWING *et al.* (1937) of the time–distance relations of the refraction lines is given below. It is of interest to us to describe these lines by their inverse slopes and their time intercepts, the problem then

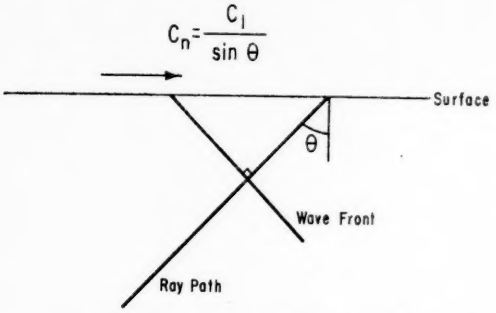

Fig. 5. Apparent velocity along a horizontal.

being to convert these two parameters into the depth, inclination, and seismic velocity of the given refractor. The inverse slope of a given refraction line determines the apparent velocity in the layer through which the sound arrivals were propagated. From Fig. 5 the measured apparent velocity for any refraction line is related to the incident angle of the refracted ray and the velocity of the medium underlying the detectors by

$$c_n = \frac{c_1}{\sin \theta} \tag{1}$$

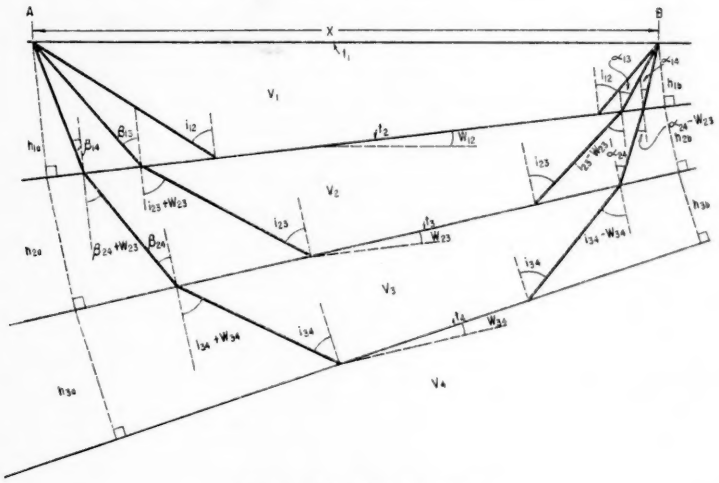

Fig. 6. Refraction ray paths.

From (1) and Snell's law we will then have for the refraction paths of the reversed profile of Fig. 6

$$
\left.
\begin{aligned}
&\frac{c_1}{c_{2a}} = \sin(i_{12} - \omega_{12}) && && \frac{c_1}{c_{2b}} = \sin(i_{12} + \omega_{12}) \\
& && \frac{c_1}{c_2} = \sin i_{12} && \\
&\frac{c_1}{c_{3a}} = \sin(\alpha_{13} - \omega_{12}) && && \frac{c_1}{c_{3b}} = \sin(\beta_{13} + \omega_{12}) \\
&\frac{c_1}{c_2} = \frac{\sin \alpha_{13}}{\sin(i_{23} - \omega_{23})} && && \frac{c_1}{c_2} = \frac{\sin \beta_{13}}{\sin(i_{23} + \omega_{23})} \\
& && \frac{c_2}{c_3} = \sin i_{23} && \\
&\frac{c_1}{c_{4a}} = \sin(\alpha_{14} - \omega_{12}) && && \frac{c_1}{c_{4b}} = \sin(\beta_{14} + \omega_{12}) \\
&\frac{c_1}{c_2} = \frac{\sin \alpha_{14}}{\sin(\alpha_{24} - \omega_{23})} && && \frac{c_1}{c_2} = \frac{\sin \beta_{14}}{\sin(\beta_{24} + \omega_{23})} \\
&\frac{c_2}{c_3} = \frac{\sin \alpha_{24}}{\sin(i_{34} - \omega_{34})} && && \frac{c_2}{c_3} = \frac{\sin \beta_{24}}{\sin(i_{34} + \omega_{34})} \\
& && \frac{c_3}{c_4} = \sin i_{34} &&
\end{aligned}
\right\} \qquad (2)
$$

where c_1 is the average sound velocity in the water, c_n the true seismic velocities of the refractors, c_{na} and c_{nb} the measured apparent velocities from the refraction lines for the receiving stations A and B, $\omega_{n-1,n}$ the inclinations of the given refractors with respect to the next overlying refractor, $i_{n-1,n}$ the critical angles for the given refractors, and $\alpha_{m,n}$ and $\beta_{m,n}$ the intermediate angles as defined in Fig. 6. The true velocities and inclinations of the respective layers can be calculated stepwise from equations (2). From the first set, knowing c_1, c_{2a}, and c_{2b} the angle ω_{12} and velocity c_2 can be determined. From the second set, knowing c_1, c_2, c_{3a}, c_{3b}, and ω_{12}, the angle ω_{23} and the velocity c_3 can be determined and so on for succeeding layers. The equations for the intercept times can be obtained from the following consideration. The intercept times are the times extrapolated back from the measured refraction line to zero range. The extrapolated ray paths would be those shown in Fig. 7. The times along these paths would be the sum of the times along the inclined paths out from A minus the time along the path parallel to the refraction horizon. For each refraction path this will be

$$
\begin{aligned}
t_{2a} &= \frac{2h_{1a}}{c_1} \cos i_{12} \\
t_{3a} &= \frac{2h_{2a}}{c_2} \cos i_{23} + \frac{h_{1a}}{c_1} (\cos \alpha_{13} + \cos \beta_{13}) \qquad (3) \\
t_{4a} &= \frac{2h_{3a}}{c_3} \cos i_{34} + \frac{h_{2a}}{c_2} (\cos \alpha_{24} + \cos \beta_{24}) + \frac{h_{1a}}{c_1} (\cos \alpha_{14} + \cos \beta_{14})
\end{aligned}
$$

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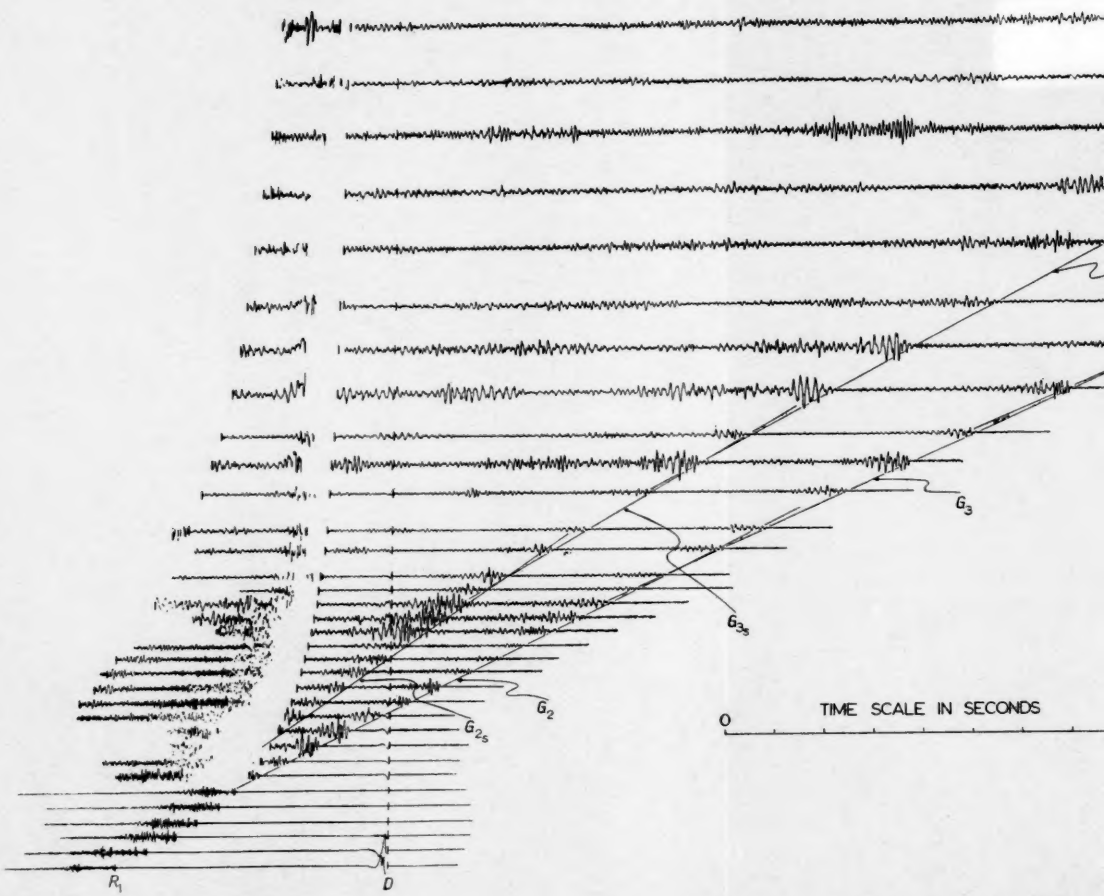
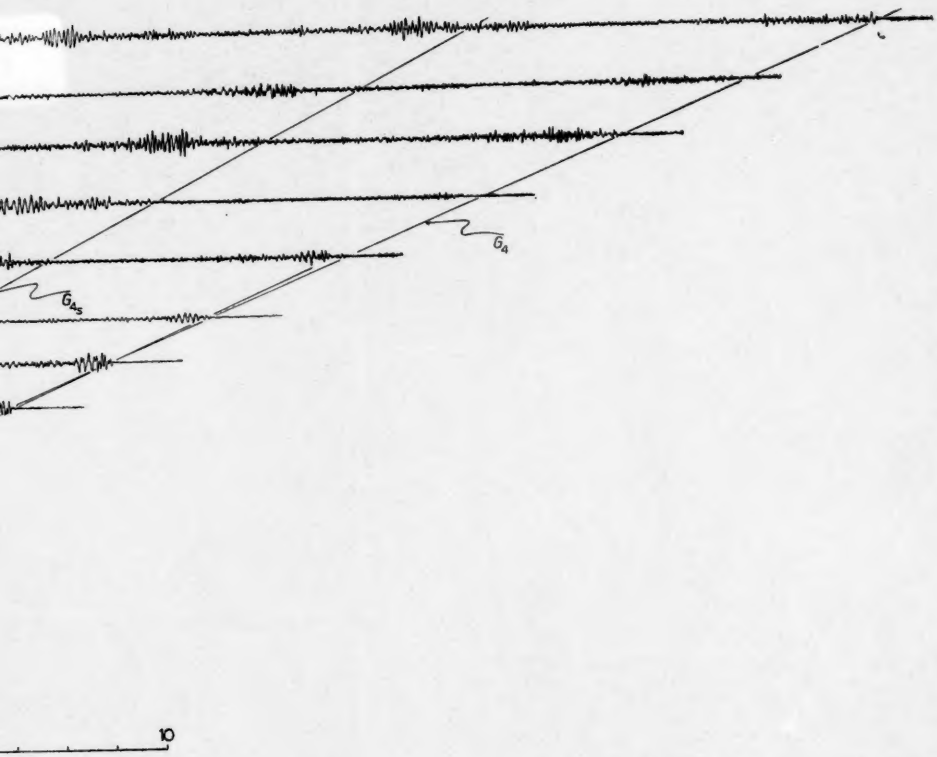


Fig. 8. Refraction seismogr



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The times t_{na} are the measured intercept times at A and the thicknesses $h_{n-1,a}$ are as defined in Fig. 7. From equations (3) the thicknesses $h_{n-1,a}$ may be calculated stepwise. From the first equation h_{1a} can be determined. From the second equation knowing h_{1a}, h_{2a} can be determined and so on. A similar set of equations exist for point B for the calculations of h_{1b}, h_{2b}, . . . The average sound velocity of the ocean, c_1, is a time average not a straight velocity average.

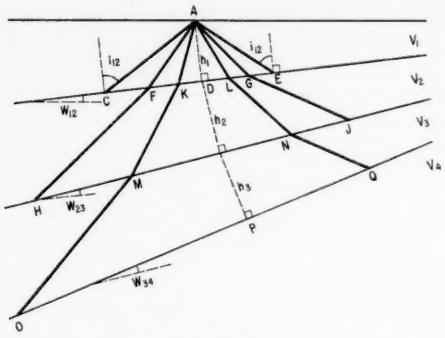

Fig. 7. Fictitious time intercept ray paths.

It is that velocity which when multiplied by half the bottom reflection time will give the true depth of water, or

$$c_1 = \frac{H}{\int_0^H \{dh/c(h)\}}$$

where H is the depth of water. Fortunately the velocity c_1 is a sufficiently slowly varying function that an average velocity may be defined over various depth ranges and areas of the ocean from the several measurements of temperature and salinity at depth. Tables of such values are available (MATTHEWS, 1939).

In principle the reading of the D and G arrivals from the refraction seismograms is straightforward; the beginning of each arrival is picked. In practice, however, as with most seismic records, the reading of the records is the most critical part of the reduction of the data. In general the D arrival offers no problems; it has a sharp, distinct beginning, easy to recognize and to read. The G arrivals are usually easy to recognize; the difficulty occurs in picking their beginnings. Some start abruptly and offer no problem. Others, however, have an emergent beginning; and care must be taken in reading them. Further, at the longer ranges the amplitudes of the refraction arrivals are generally small, offering in some cases difficulties in reading their beginnings from the associated noise background.

In reading the records emphasis is on the beginning of the first refraction arrival. As shown in Fig. 12, the first refraction arrival progresses from one refraction line to the next (representing successively deeper layers) with succeeding range so that a detailed shot schedule will usually allow a good determination of each line from first arrivals. Later refraction arrivals after the first are picked when they can be recognized and followed from one record to the next; the

difficulty there is in picking the beginning of these later arrivals out of the wave train from the preceding refraction arrival. The appearance of the various arrivals is shown in Fig. 8 where one low frequency trace from each record at profile 26 *N* was duplicated and spaced according to shot distance to demonstrate the correlation of the different phases.

A number of corrections must be made to the *D* and *G* arrivals read from the seismograms before the final travel time plots can be made. These are the shot instant correction, surface of reference correction, and topographic correction. The first correction applies to all readings, the later two to only the *G* readings. The shot instant correction is simply the interval of time it took the sound to travel from the shot point to the echo sounder transducer on the shooting ship.

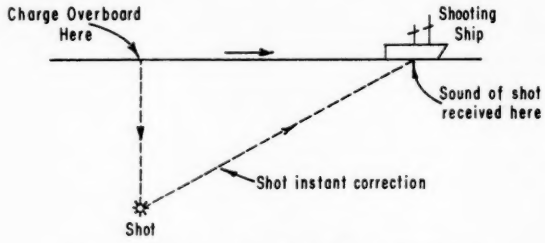

Fig. 9. Ray diagram for shot instant correction.

It is the correction to the instant of detonation from the zero of time used on the seismograms. From Fig. 9 it is simply

$$\Delta t_{si} = \frac{\{(V_{ss}\Delta T_{os})^2 + (\Delta d_s)^2\}^{\frac{1}{2}}}{c_0} \tag{4}$$

where V_{ss} is speed of the shooting ship, T_{os} the time interval that the charge was in the water before detonation, and Δd_s the depth of the shot. V_{ss} is determined sufficiently accurately from the slope of a plot of uncorrected *D* vs. the absolute time of the instant of detonation. Every explosion at moderate depths in the ocean will have one or more bubble pulses. The bubble pulses are simply the oscillations of the gas bubble and appear on the records as second shots. The time interval between the instant of detonation and the first bubble is dependent on the charge size, kind, and depth (pressure). The relation between this interval and the depth at which the charge has been detonated has been determined empirically for various size TNT charges (EWING *et al.*, 1946). The quantity Δd_s was determined from such an empirical plot. An alternative method in deep water for the deeper shots was to measure the time interval between the first bottom reflection and the arrival immediately following which had been reflected once from the ocean surface above the shot and then from the bottom; the shot depth is then simply one-half this time interval multiplied by the sound velocity. The surface of reference correction is made to refer all data to the same reference surface for calculations. This surface is taken as the ocean surface. From Fig. 10 this is the time interval between the two wave-fronts shown, or

$$\Delta t_{sr} = \frac{\Delta d_s}{c_0} \cos\left(\sin^{-1}\frac{c_1}{c_{na}}\right) + \frac{\Delta d_H}{c_0} \cos\left(\sin^{-1}\frac{c_1}{c_{nb}}\right) \tag{5}$$

for the A portion of a reversed profile where Δd_H is the depth of the receiving hydrophone. For this correction the use of the apparent velocities from the uncorrected travel time plot is sufficiently accurate. The depth Δd_H is small, less than 100 ft, so that only in the most exceptional case will the use of c_{na} for c_{nb} in the second term of (5) cause a measurable difference. The topographic

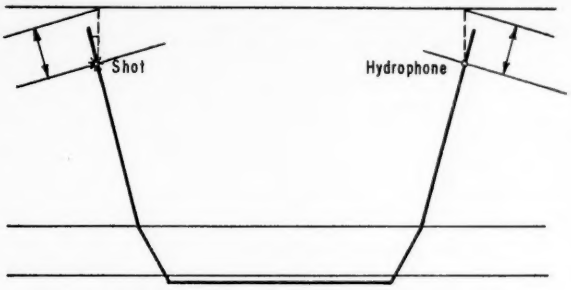

Fig. 10. Ray diagram for surface of reference correction.

correction is the correction for variations in arrival times due to variations in the bottom topography. The refraction equations derived above were for planar refracting surface. Variations in the thickness of any of the layers above the particular refractor will cause deviations of the plotted points away from the assumed straight lines. It is desirable to remove the deviations due to bottom

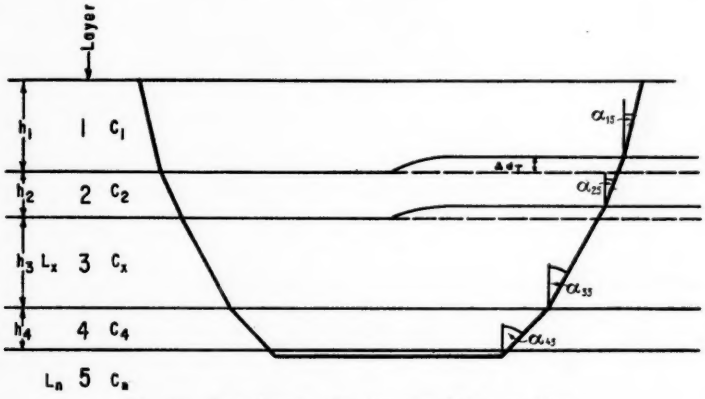

Fig. 11. Ray diagram for topographic correction.

topography before making the final travel time plot. The net effect of changes in bottom topography, as shown in Fig. 11, may be considered to be changes in the intercept times of the theoretical refraction line. For a change in the bottom topography of Δd_T which is caused by a layer of seismic velocity c_x the topographic correction will be

$$\Delta t_T = \frac{\Delta d_T}{c_1} \cos\left(\sin^{-1}\frac{c_1}{c_{na}}\right) - \frac{\Delta d_T}{c_x} \cos\left(\sin^{-1}\frac{c_x}{c_{na}}\right) \tag{6}$$

for the A portion of a profile. The velocity c_x is generally taken as the first high velocity refractor beneath the bottom. This is an assumption, but reasonable changes in the velocity c_x away from this value will generally cause a negligible error. The quantity Δd_T is measured above or below a mean bottom base line, either inclined or horizontal, as determined from the shooting ship's echo sounder record. The quantity Δd_T is not measured directly beneath the shot point but at the offset distance, R, given by

$$R = H \tan \left(\sin^{-1} \frac{c_1}{c_{na}} \right) \tag{7}$$

The corrected G and D arrivals are plotted to give the final travel time plot and are fitted with the appropriate refraction lines. This fitting is not done by a

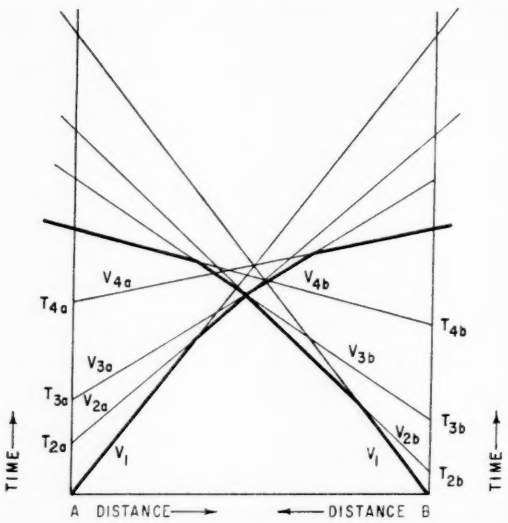

Fig. 12. Sketch of normal refraction travel time graphs.

least squares or other such means but by a qualitative weighting of each point on the line. It is almost always true that a fit to the data by a small number of well defined lines is as good a fit as can be made. The points usually follow one line and then diverge to a second line; it is seldom that one would prefer to fit a group of arrivals by a curve. Such straight line travel time plots are caused by discontinuous or rapid changes in the seismic velocity as a function of depth as contrasted to a continual gradual change in velocity. On reversed profiles the two corresponding refraction lines from the A and B receiving locations give a unique determination of the depth, inclination, and seismic velocity of the particular refracting layer. However, on the longer profiles presented here the arrivals from the shallow refractors do not cover the same portion of the refracting horizon on both the A and B portions. The inclination of such a layer may change between the two portions, and a unique solution cannot be obtained. This may be partially resolved by the agreement of the reverse points, i.e., the travel time at the reverse distance, of the two corresponding lines. The deeper

layers generally give good reverses. On unreversed profiles or unreversed lines of a reversed profile an assumption must be made for the inclination of the refracting horizon in order to carry out the calculations for velocity and depth. The refraction line sequence for a normal reversed profile will be as sketched in Fig. 12. Over some portion of each refraction line below the bottom the refraction arrival will appear as the first arrival on the refraction seismograms. With a sufficiently detailed shot schedule each line can be well determined from the first arrivals. On some profiles, however, the refraction line for a layer at great depth may not appear as a first arrival, as shown in Fig. 13; such a layer

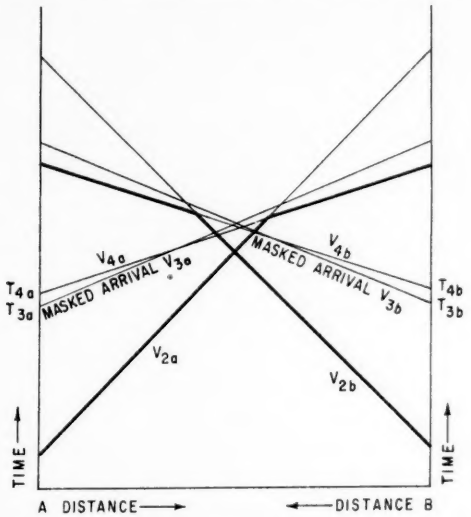

Fig. 13. Sketch of masked layer refraction travel time graph.

is referred to as being masked. The presence of such a line can generally not be determined from the seismograms; its identification can only be given from the measurement of second arrivals. It is judged that there is a masked layer on three of the longer 1956 profiles in the vicinity of the Puerto Rico trench. The first refraction line on most of the deep-water profiles of both cruises did not correspond to a refraction through the material immediately beneath the ocean bottom but to a higher velocity refractor at greater depth. In such cases it is necessary to assume a seismic velocity for the unconsolidated sedimentary material above the first refractor. Since the thickness of this undetermined sedimentary material is generally thin, possible variations in the assumed velocity from the true velocity cause little error in the calculations of the depths of the deeper horizons. For most of the deep water profiles this velocity was taken from a relation for sedimentary velocity vs. depth determined from an analysis of the sub-bottom reflection profiles from these Caribbean profiles.

GEOPHYSICAL RESULTS

The geophysical results are presented in Fig. 2 and in Table 1. Each figure of Fig. 2 contains the corrected travel time plot with the plotted points for each

Table 1. Measured Seismic Velocities and Thicknesses

Profile 1				Profile 2		Profile 3		Profile 4		Profile 5			
T_W	V_W	V_E	T_E	T_N	V_N	T_W	V_W	T_W	V_W	T_W	V_W	V_E	T_E
0·03	1·53		0·03	4·21	1·51	1·36	1·50	0·95	1·50	0·08	1·53		0·08
0·04	1·97		0·41	1·54	(2·14)	1·37	[2·32]	3·13	(2·32)	0·07	1·67		0·36
	2·56				(3·80)		(4·48)		(5·27)	1·04	2·17		1·52
											5·72		

Profile 6		Profile 7			Profile 8			Profile 9			Profile 10	
T_S	V_S	T_S	V_S	V_N	T_N	T_W	V_W	V_E	T_E	T_W	V_W	V_E	T_E	T_S	V_S
0·08	1·53	4·22	1·51		3·50	3·94	1·51		3·67	3·21	1·50		3·06	1·28	1·50
							1·72				1·78				
0·46	(1·84)	3·10	⟨2·67⟩		3·54	2·14	⟨2·38⟩		2·35	0·90	⟨1·75⟩		0·31	0·70	[1·80]
1·09	(2·19)	6·74	5·84		4·43	2·85	4·82		2·27	1·45	2·83		1·60	0·60	[3·40]
	(5·96)		7·38				6·85			2·25	4·06		2·90	1·61	(4·90)
											6·68				(6·20)

Profile 11				Profile 12				Profile 13				Profile 14				Profile 15	
T_N	V_N	V_S	T_S	T_W	V_W	V_E	T_E	T_N	V_N	V_S	T_S	T_W	V_W	V_E	T_E	T_S	V_S
0·08	1·54		0·08	0·09	1·52		0·95	1·10	1·50		0·82	0·82	1·50		1·54	0·73	1·50
0·05	1·76		0·13	0·11	1·71		0·61	1·30	[1·70]		1·30	1·31	[1·70]		1·48	0·78	(1·81)
0·96	2·68		0·77	0·67	2·39		0·18	3·48	4·33		2·96	2·63	4·19		3·20	2·18	(2·50)
0·41	3·44		0·88	0·85	3·25		1·25		5·30				5·35				(3·38)
0·62	4·40		2·49	2·56	4·29		1·51										
	6·31				5·97												

⟨ ⟩—sedimentary velocity from refl. prof. ( )—unreversed velocity. [ ]—assumed velocity.
All depths in kilometres and all velocities in kilometres per second.

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Table 1. Measured Seismic Velocities and Thicknesses—continued

Profile 16				Profile 17				Profile 18				Profile 19				Profile 20			
T_S	V_S	V_N	T_N	T_W	V_N	V_E	T_E	T_N	V_N	V_S	T_S	T_E	V_E	V_W	T_W	T_N	V_N	V_S	T_S
1·09	1·50		0·37	2·85	1·50		4·07	5·05	1·51		4·84	2·37	1·50		2·01	1·27	1·50		2·10
													[1·70]						
0·27	[1·72]		0·38	0·54	[1·70]		1·20	0·25	[1·70]		0·10	2·38	1·91		0·67	1·63	[1·70]		0·87
0·51	2·22		2·00	6·21	2·58		2·62	1·98	2·23		3·13	2·87	2·41		5·37	4·00	[2·00]		—
3·32	3·21		5·20	6·79	6·74		5·79	6·29	6·68		4·94	3·10	4·31		3·92	2·23	(2·95)		2·23
	4·27				8·32				8·13				(6·77)				3·70		

Profile 21				Profile 22				Profile 23		Profile 24				Profile 25	
T_N	V_N	V_S	T_S	T_N	V_N	V_S	T_S	T_S	V_S	T_N	V_N	V_S	T_S	T_E	V_E
2·19	1·50		2·19	1·10	1·50		1·23	0·14	1·50	0·14	1·52		0·10	0·13	1·52
									[1·66]		[1·66]				[1·70]
0·35	[1·70]		0·51	1·07	[1·70]		0·32	1·08	(2·01)	1·08	1·93		0·90	1·37	(2·01)
3·13	1·93		1·66	2·56	3·97		2·82	2·51	(2·71)	2·51	2·75		0·37	2·95	(2·93)
4·70	3·81		3·39		4·91			0·34	(3·68)	0·34	3·43		1·74	2·18	(5·20)
	5·31							2·19	(5·10)	2·19	4·80		3·03		(6·47)
									(6·83)		6·38				

Profile 26		Profile 27				Profile 28		Profile 29				Profile 30			
T_E	V_E	T_S	V_S	V_N	T_N	T_S	V_S	T_S	V_S	V_N	T_N	T_S	V_S	V_N	T_N
0·16	1·51	0·16	1·51		0·68	0·04	1·51	2·93	1·50		2·93	1·30	1·50		1·48
	(1·64)		1·64						(2·01)						
1·26	(2·03)	1·26	2·03		1·66	0·06	[1·70]	2·81	⟨2·52⟩		1·60	0·78	⟨1·84⟩		0·00
2·35	(2·57)	2·35	2·57		1·93	1·34	(2·33)	2·55	(3·76)		1·80	1·53	3·66		1·57
	(4·33)		4·33			3·05	(4·00)	2·24	(5·28)		1·39	2·58	4·42		3·63
							(6·40)	7·85	6·22		6·40	3·05	6·15		2·71
									7·41				6·69		

⟨ ⟩—sedimentary velocity from refl. prof. ( )—unreversed velocity. [ ]—assumed velocity.
All depths in kilometres and all velocities in kilometres per second.

Table 1. Measured Seismic Velocities and Thicknesses—continued

Profile 31				Profile 32				Profile 33				Profile 34				Profile 35			
T_E	V_E	V_W	T_W	T_E	V_E	V_W	T_W	T_E	V_E	V_W	T_W	T_S	V_S	V_N	T_N	T_W	V_W	V_E	T_E
3·44	1·50		4·28	4·45	1·51		4·45	5·02	1·51		5·02	3·28	1·50		1·59	0·02	1·53		0·02
	1·82								(2·05)				(1·95)						
0·82	⟨1·79⟩		1·29	1·07	⟨1·93⟩		0·80	—	⟨1·71⟩		0·41	0·82	⟨1·84⟩		0·50	0·75	1·95		0·37
1·06	(2·79)		1·00	0·97	3·84		2·38	2·19	(3·15)		2·83	5·36	3·75		0·76		5·23		
3·57	4·22		1·06	8·34	6·71		6·88	3·27	5·12		1·21		4·79						
2·29	6·41		3·87		8·04			2·95	6·92		9·00								
7·10	7·13		4·31						7·78										
	8·31																		

Profile 36				Profile 37				Profile 38				Profile 39				Profile 40			
T_W	V_W			T_S	V_S	V_N	T_N	T_W	V_W	V_E	T_E	T_S	V_S	V_N	T_N	T_S	V_S	V_N	T_N
1·88	1·50			0·01	1·53		0·01	4·34	1·51		4·34	1·35	1·50		1·04	1·09	1·50		0·82
	(1·97)																		
0·87	⟨1·93⟩			0·25	[1·96]		0·09	0·65	⟨1·65⟩		0·01	0·91	(1·92)		0·48	0·40	[1·70]		0·46
1·16	(4·94)				5·00			1·73	3·07		2·57	1·86	2·95		0·97	1·02	(2·92)		0·60
4·99	(5.63)							4·09	5·77		1·63		5·37				5·70		
	(7·98)								7·33										

Profile 41				Profile 42				Profile 43				Profile 44				Profile 45			
T_S	V_S	V_N	T_N	T_W	V_W	V_E	T_E	T_W	V_W	V_E	T_E	T_E	V_E	V_W	T_W	T_E	V_E	V_W	T_W
0·82	1·50		0·71	5·94	1·52		5·94	6·31	1·52		5·95	6·17	1·52		6·17	6·81	1·53		6·81
					(2·36)														
0·46	[1·70]		0·52	2·29	⟨2·55⟩		2·96	0·25	⟨1·77⟩		0·96	0·66	⟨1·70⟩		0·17	2·84	⟨2·50⟩		0·00
0·60	2·34		0·63		5·86			2·09	3·49		1·31	0·24	4·51		2·46	0·00	4·28		1·61
	5·24								5·45			6·91	6·62		2·90	1·97	5·50		1·01
													7·85			4·77	6·24		6·70
																	8·05		

⟨ ⟩—sedimentary velocity from refl. prof. ( )—unreversed velocity. [ ]—assumed velocity.
All depths in kilometres and all velocities in kilometres per second.

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Table 1. Measured Seismic Velocities and Thicknesses—continued

1955 *and* 1956 *Profiles*

Profile 46				Profile 47				Profile *1*				Profile *2*				Profile *3*			
T_E	V_E	V_W	T_W	T_N	V_N	V_S	T_S	T_N	V_N	V_S	T_S	T_N	V_N	V_S	T_S	T_W	V_W	V_E	T_E
7·87	1·53		8·15	8·38	1·53		8·38	5·87	1·52		5·87	5·86	1·52		5·74	5·49	1·51		5·49
2·45	3·38		2·12	0·21	⟨1·94⟩		1·37	0·48	⟨1·75⟩		—	0·58	⟨1·77⟩		0·39	0·36	⟨1·73⟩		0·50
7·97	6·33		7·12	1·41	4·70		1·65			(4·22)	1·48	1·25	5·96		1·70	3·01	5·70		1·67
	7·94				7·13			5·80	6·87		7·11	3·92	6·93		4·00	4·94	7·11		3·31
									8·21				7·96				8·44		
Profile *4*				Profile *5*				Profile *6*				Profile *7*				Profile *8*			
T_N	V_N	V_S	T_S	T_S	V_S	V_N	T_N	T_S	V_S	V_N	T_N	T_S	V_S	V_N	T_N	T_E	V_E	V_W	T_W
5·91	1·52		6·14	6·41	1·52		6·41	5·58	1·52		5·58	4·78	1·51		4·78	0·66	1·54		0·66
0·51	⟨1·81⟩		0·60	2·55	⟨2·38⟩		1·95	0·25	⟨1·58⟩		0·08	3·44	⟨2·46⟩		1·02	1·08	1·97		1·09
1·97	5·66		2·90	1·03	5·44		4·03	1·21	2·56		1·34		5·27		(1·89)	1·95	3·80		1·22
6·31	6·92		4·33	4·94	6·98		5·09	4·10	3·52		2·51		(6·06)			3·16	5·19		2·19
	8·36				8·64			2·32	4·75		4·34						6·26		
								4·66	[6·62]		6·39								
									8·35										
Profile *9*				Profile *10*				Profile *11*				Profile *12*				Profile *13*			
T_N	V_N	V_S	T_S	T_N	V_N	V_S	T_S	T_W	V_W	V_E	T_E	T_W	V_W	V_E	T_E	T_W	V_W	V_E	T_E
1·68	1·54		4·22	4·22	1·54		4·22		1·54		2·09	2·09	1·54		1·34	0·91	1·54		1·28
1·18	[2·04]		0·90	0·74	2·04		1·37			(1·82)	0·22	—		[1·70]	0·30	0·63		[1·72]	0·71
0·48	2·94		1·27	1·57	(3·14)		0			(2·30)	1·09	0·22	1·82		0·65	1·56		(2·45)	0·71
0·64	3·73		2·18	1·80	3·97		0·63			(3·75)	1·56	1·09	2·30		0·21	1·03		(3·98)	2·48
6·07	5·06		0·14	9·53	6·13		4·11			(6·04)		1·56	3·75		1·72			(5·42)	
	[5·99]				7·58								6·04						

⟨ ⟩—sedimentary velocity from refl. prof. ( )—unreversed velocity. [ ]—assumed velocity.

All depths in kilometres and all velocities in kilometres per second.

Table 1. Measured Seismic Velocities and Thicknesses—continued

1955 *and* 1956 *Profiles*

Profile *14*				Profile *15*				Profile *16*				Profile *17*				Profile *18*			
T_W	V_W	V_E	T_E	T_W	V_W	V_E	T_E	T_N	V_N	V_S	T_S	T_N	V_N	V_S	T_S	T_N	V_N	V_S	T_S
1·28	1·54		0·70	0·70	1·54		0·70	0·04	1·54		0·04	6·46	1·52		5·30	7·83	1·53		5·41
0·71	1·72		0·44	0·38	[1·72]		0·05	0·19	(2·08)		0·10	0·15	⟨1·68⟩		0·61	0·26	⟨1·64⟩		0·15
0·71	2·45		0·91	1·33	2·68		0·98	0·35	2·72		0·97	1·46	(2·04)		—	—		(3·48)	2·02
2·50	3·98		1·95	1·40	3·66		1·08	1·60	4·78		3·88	—		(3·85)	4·91	5·94	4·62		11·87
	5·41				5·23				6·23			5·55	5·48		6·70	3·67	[6·68]		4·18
												6·35	6·76		3·46		8·30		
													8·42						
Profile *19*				Profile *20*				Profile *21*				Profile *22*				Profile *23*			
T_N	V_N	V_S	T_S	T_E	V_E	V_W	T_W	T_N	V_N	V_S	T_S	T_N	V_N	V_S	T_S	T_N	V_N	V_S	T_S
0·06	1·54		0·06	6·02	1·52		6·02	1·21	1·54		1·94	1·74	1·54		1·41	1·41	1·54		1·22
0		(2·00)	0·38	0·04	⟨1·58⟩		0·18	1·04		(1·66)	0·83	0·73	1·67		0·62	0·67	1·65		0·77
0·63	(2·86)		0	2·63	3·66		2·17	1·12	2·61		1·38	2·51	3·23		1·30	0·96	2·90		0·88
1·41	3·83		1·61	10·05	5·55		9·18	3·78	5·44		1·76	0·87		(4·98)	2·77		4·70		
2·57	5·64		5·31	3·43	[6·79]		3·94	4·13	5·95		2·75		6·24						
	6·49				8·43				6·52										

⟨ ⟩—sedimentary velocity from refl. prof. ( )—unreversed velocity. [ ]—assumed velocity.
All depths in kilometres and all velocities in kilometres per second.

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Table 1. Measured Seismic Velocities and Thicknesses—continued

1955 *and* 1956 *Profiles*

Profile *24*				Profile *25*				Profile *26*			
T_E	V_E	V_W	T_W	T_E	V_E	V_W	T_W	T_N	V_N	V_S	T_S
3·41	1·54		4·41	4·92	1·54		5·02	4·95	1·54		4·95
0·49	1·70		0·37	0·63	[1·70]		0·91	0·75	1·73		1·45
0·40	(2·35)		0·60	0·03	2·05		0·14	4·25	5·99		1·77
1·93	(3·21)		0·74	1·99	(2·73)		1·63	5·08	7·21		4·55
1·94	(4·95)		1·10	2·11	6·23		2·16		8·20		
5·32	6·15		5·10	2·95	7·63		3·05				
4·51	7·36		5·75		8·23						
	8·08										

Profile *27*				Profile *28*				Profile *29*				Profile *30*			
T_N	V_N	V_S	T_S	T_E	V_E	V_W	T_W	T_E	V_E	V_W	T_W	T_E	V_E	V_W	T_W
4·46	1·54		4·46	0·03	1·54		0·03	3·67	1·51		3·67	0·04	1·54		0·05
0·84	[1·80]		0·42	0·10	1·89		0·17	0·79	⟨1·91⟩		0·77	0·15	1·98		0·29
1·28	3·32		1·74	0·17	2·90		0·51	2·64	4·96		1·65	0·72	2·85		1·03
2·76	6·51		2·93	5·74	5·71		4·15	8·30	6·05		3·93	0·89	4·55		3·86
5·75	7·11		5·50		6·61				7·03			11·60	5·75		5·37
	7·92												6·98		

⟨ ⟩—sedimentary velocity from refl. prof. ( )—unreversed velocity. [ ]—assumed velocity.
All depths in kilometres and all velocities in kilometres per second.

shot and the fitted refraction lines from which the calculations were made, the bottom topography for each shooting ship track, and the computed seismic section. Table 1 is a tabulation of the computed thicknesses and velocities for each layer. Along each refraction line in each of the figures its equation has been written in the form

$$G = \frac{D}{4{\cdot}56} + 1{\cdot}23 \tag{8}$$

The dependent variable is the G travel time and the independent variable the D travel time. The number, 4·56, is the inverse slope with respect to D; the apparent velocity c_{na} is this number multiplied by c_0. The number, 1·23, is the time intercept t_{na}. The 1955 results presented by OFFICER *et al.* (1957) did not have topographic corrections; these profiles have been reanalysed here and some changes in the results do occur. In particular the long range Venezuelan basin profiles 31, 32, and 33 are now interpreted as having an additional deeper horizon whose velocity is slightly higher than that of the deepest horizon in the previous interpretation. The pertinent features of each of the profiles is discussed below. Their locations are given in Fig. 1 and the measured seismic velocities and thicknesses are given in Table 1.

1, 2, 3, 4. All these profiles are short and unreversed. They provide little information.

5, 6. Require no comment.

7. The drift of the *Atlantis* at the northern end of the profile was considerably greater than that for the *Caryn* at the southern end. The reverse shooting track of the *Caryn* was not true. The profile was long but was not heavily shot. No velocity above 7·38 km/sec was determined; this is probably due to the sparsity of points on the travel time graph rather than the absence of higher velocities at the depths corresponding to the distance of coverage of this profile.

8, 9. These were short reversed profiles. All velocities are well determined, but the profiles are not long enough to detect the mantle.

10. This is an unreversed profile. The true velocities used in the calculations were chosen to agree with nearby profiles 30, *22*, and *23*.

11, 12. The quality of the *Caryn* records in these profiles is sub-normal, particularly in part of profile 11, but owing to the mutual support obtained by having the profiles end-to-end, the results should be reasonably reliable.

13, 14. These profiles are well shot and have the control furnished by end-to-end reversed profiles, but there is still enough scatter of the points to make the interpretation somewhat uncertain in detail. For example, the reverse points in profile 14 fail to agree by almost 0·4 sec. This discrepancy can be attributed to an excessive delay between shooting the two halves of the profile producing a large offset in the two shooting tracks.

There is evidence from reflection data of a higher velocity sediment layer approximately 0·5 km below the ocean floor. This could be the 2·2–2·8 km/sec layer found in the neighbouring profiles and is assumed in Section 8, Fig. 21. Because of the scattering of the points in these profiles, the velocity in the deepest layer may not be determined accurately. Comparison with profile 26 (previous profiles) and profiles 11 and 12 suggest that either the velocity determination is substantially low or else the 5·3 km/sec layer is thin.

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15. This profile has well determined lines but is unreversed and gives only apparent velocities.

16. Most of the lines on the travel time graph are reasonably well determined and reverse satisfactorily, although the scattering of the points, particularly on the high velocity lines, indicates a considerable amount of relief in the deeper interfaces.

17. This profile measures the thick sedimentary section on the eastern flank of the Barbados ridge and shows the westward dip of the high-velocity layers. Possibly some of the 4–5 km/sec material found in the Barbados ridge is present at the west end of this profile. Although it was not seen as a refractor it could be masked by the great thickness of low velocity material.

18. This profile, as presented by EWING *et al.* (1957), did not properly take into account the effects of the topographic rise at the south end and has been recomputed for this paper. The first computation showed more dip in the deep interface. The results here, although showing considerably more sedimentary material, are typical of ocean basin profiles. The lines, G_8, are determined by transformed shear waves.

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19. The interpretation of this profile was complicated, and the results given by it are very uncertain. Although no arrivals could be picked in the *Caryn* records to fit the G_5 line, it was assumed that they were too weak to be seen. Any alternate structural interpretation which would fit the data and even approximately satisfy the conditions for a reversed profile, requires a very large fault or flexure near one end of the profile (west side down relative to the east side).

20. This profile shows a very large fault or steep flexure near the north end. An alternate interpretation might be considered wherein it would be assumed that the last three points in the Atlantis profile and all the points in the *Caryn* profile came from multiply refracted arrivals. It is very improbable, however, that all the first arrivals in the *Caryn* records could have been missed, since there was normal sensitivity and no unusual noise.

21. Although the upper layers in this profile are satisfactorily determined, the velocity in the deepest one is not. On the basis of two very weak records (points not plotted) between the last two in the *Caryn* profile, there is some possibility of increasing the velocity in the deepest layer by a small amount, thereby slightly increasing the depth to that layer at the south end.

22. This is a long profile, but the shots at the greater distances were not large enough to penetrate to the deeper layers. The scatter of points indicates a rather large amount of relief in the layers. Perhaps complexity in the layering, as well as, or rather than great thickness prevented the detection of arrivals from deeper layers. The dashed lines G_4 were drawn to compute the minimum depth to a velocity of 6·5 km/sec, assuming that the longest recorded shots were large enough to penetrate to the required depth but that the range was not sufficient to give a first arrival from such a layer. The computed minimum depth is 12 km, but there is not much significance attached to it in such a complicated area as this.

23, 24. This end-to-end pair consists of one unreversed and one reversed profile. The layer thicknesses at the north end of 23 were computed on the assumption that the velocity in each layer does not change appreciably between the two profiles. The high point on the end of the G_6 line probably represents a downward flexure or fault in the 6·4 km/sec layer. This layer was not detected

at profiles 26 and 27, a few miles further north, presumably because of its great depth, and it is unfortunate that profile 23 was not longer to provide more confirmation of this depth.

25. This is a long unreversed profile shot approximately parallel to the northern coast of Trinidad and Venezuela. The layer thicknesses were computed on the assumption that there was no component of dip in the direction of the profile.

26, 27. The most significant feature of these profiles is their failure to detect the 6·0–6·5 km/sec crustal layer, which is found at a depth of 4–6 km near Grenada and Trinidad. Minimum depth computations for profile 27, which is relatively long and heavily shot, give a depth of at least 12 km to this layer. This is the evidence on which the synclinal feature shown in Section 9 was based.

28. This unreversed profile was shot along the Lesser Antilles arc between Grenada and St. Vincent. Although only apparent velocities were measured, probably these are not seriously effected by slope since the shot line is approximately parallel to the structure of the arc. The section for this profile does not show the structure indicated by the offset in the G_3 line at about 27 sec of D time. This effect can be accounted for by either an elevation (north relative to south) of the 6·4 km/sec layer or an elevation of both the 4·0 and the 6·4 km/sec layers. In the former case, an elevation of 3 km is required, which would bring the top of the 6·4 layer approximately to the level of the top of the 4·0 layer as it appears in the section. The latter case requires the elevation of both the lower layers approximately 1·5 km, which would raise the 4·0 km/sec layer to about water depth, i.e. there would be a negligible thickness of the lower-velocity materials at the north end of the profile.

29. The *Atlantis* segment of this reversed profile gave a good determination of all the velocity layers. The *Caryn* reverse was not completed and only gave a reversed profile for the two highest velocity lines.

30. Requires no comment.

31. A reinterpretation of this profile was made. The topographic corrections made a considerable change in the higher velocity lines, showing an additional line with velocity 8·31 km/sec. The solution given here is more compatible within itself and is more in agreement with nearby profiles than the solution given previously by OFFICER *et al.* (1957).

32. A reinterpretation of this profile, particularly of the arrivals determining the highest velocity line, indicated that the highest velocity could be drawn with a higher velocity, 8·04 km/sec, than that given previously. The arrivals at the longer ranges, necessary for a good determination of this line, were weak; their beginnings could not be determined accurately.

33. A reinterpretation of this profile, including topographic corrections, made a considerable change in the velocity and configuration of the higher velocity layers. The arrivals on the highest velocity line were weak; the line is not well determined.

34. The topographic slope is steep. The profile is short, but the underlying configuration is well determined. There is a considerable difference in the apparent velocities of the two sides of the reverse.

35, 37. Require no comments.

36. This is a well determined unreversed profile. The highest velocity line probably does not represent a true seismic velocity. A change in the assumed

slope, needed for velocity calculation, would give a lower velocity than that shown in Table 1.

38. The lines are well determined. A masked arrival line, given in the previous interpretation, was not included here.

39, 40, 41. These form three end-to-end, reversed profiles. Only one high velocity line was determined. The profiles give a good determination of the change in configuration of this surface along the surveyed line.

42. Corrections for the large change in topography across the profile provided nearly straight lines. Only one velocity line was measured.

43. Similar to 42 only one velocity line was determined. This was a long profile; and only the first high velocity line, near the ocean bottom was measured. These two profiles are approximately over the negative gravity anomaly minimum, where the 5·5–5·8 km/sec layer is presumed to be thickest.

44. This is a well determined profile in the northern portion of the Puerto Rico trench. Topographic corrections removed most of the scatter of the observed points from the determined lines.

45. This is a well determined profile. The displacement of the velocity lines on both halves of the reversed profile is interpreted as a fault as shown.

46. Requires no comment.

47. This profile was shot normal to the axis of the trench. The large change in topography caused complications in the interpretation. The profile was short, but large charges, 300 lb of TNT, had to be used for the more distant points in order to get readable refraction seismograms. This is to be compared with 25 lb of TNT for the same distance on profile 46.

1. The topography from both ships shows an abrupt peak about $\frac{1}{2}$ km high. This is formed by the 4·22 km/sec material. The last point on each line falls well above the highest velocity line.

2. The effect due to the change in topography on the *Bear* shooting track was removed by a topographic correction. The points define well determined lines.

3. The effects due to the change in topography on both shooting tracks was removed by a topographic correction. The points define well determined lines.

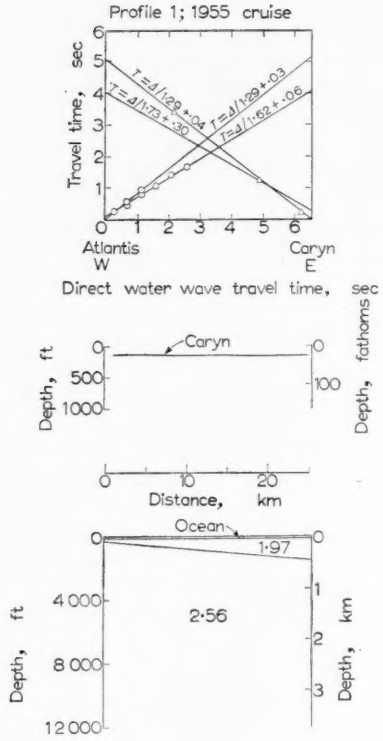
4, 5. Require no comment.

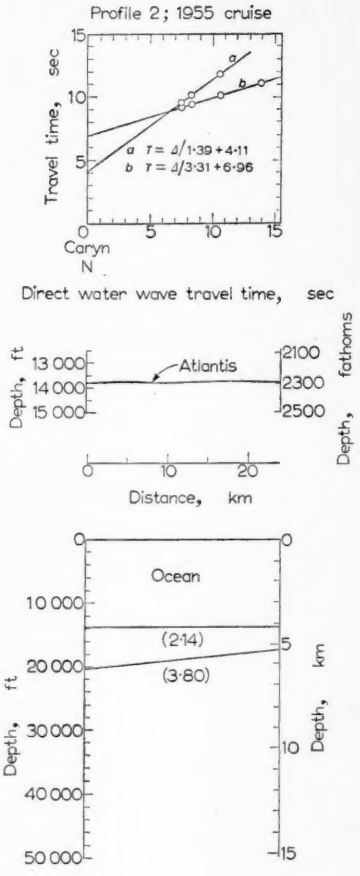
6. The overlying materials with velocities 2·56, 3·52 and 4·75 km/sec are thick under this profile. The dashed lines are the masked or nearly masked velocity lines for the crustal refraction arrival. It has been included in the depth calculation.

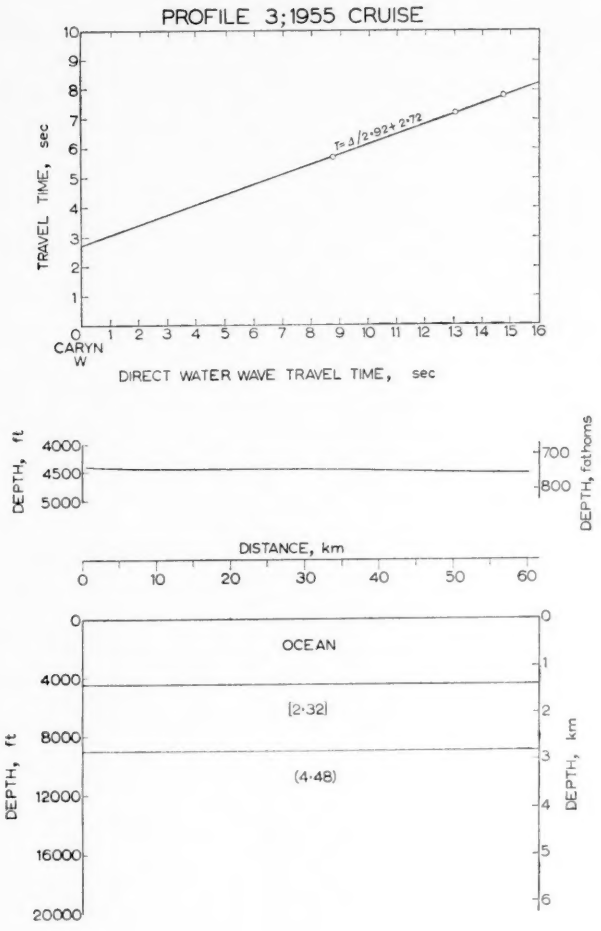
7. This is a poor profile. The arrivals are weak and do not give well defined lines.

8. Topographic corrections were applied assuming the bottom to be level at 360 fathoms and all interfaces parallel. The residuals indicate that there is a considerable amount of relief in one or more of the deeper layers. The structure section was drawn to correspond to the assumed structure. Actually all interfaces on the west end are deeper by the amount of increased water depth.

9, 10. Topographic corrections were applied for a level base line at 2240 fathoms for profile *10* and to a sloping base line paralleling the topography in profile *9*. All interfaces are actually about 0·8 km. higher than shown at the north end of the section. The accuracy is probably not high in profile *9* due to the steep slope. The lines have been drawn to give the best fit of the points, as well as to produce a satisfactory agreement with profile *10*. The velocity in the


Profile 1; 1955 cruise
Travel time, sec
T = Δ/1·28 + ·04
T = Δ/1·73 + ·30
T = Δ/1·29 + ·03
T = Δ/1·62 + ·06
Atlantis W
Caryn E
Direct water wave travel time, sec
Caryn
Depth, ft
Depth, fathoms
Distance, km
Ocean
1·97
2·56
Depth, km


Profile 2; 1955 cruise
Travel time, sec
a T = Δ/1·39 + 4·11
b T = Δ/3·31 + 6·96
Caryn N
Direct water wave travel time, sec
Atlantis
Depth, ft
Depth, fathoms
Distance, km
Ocean
(2·14)
(3·80)
Depth, km


PROFILE 3;1955 CRUISE
TRAVEL TIME, sec
T=Δ/2·92+2·72
CARYN
W
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
4000
4500
5000
700
800
DEPTH, fathoms
DISTANCE, km
0
10
20
30
40
50
60
OCEAN
[2·32]
(4·48)
DEPTH, ft
4000
8000
12000
16000
20000
DEPTH, km
1
2
3
4
5
6

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3
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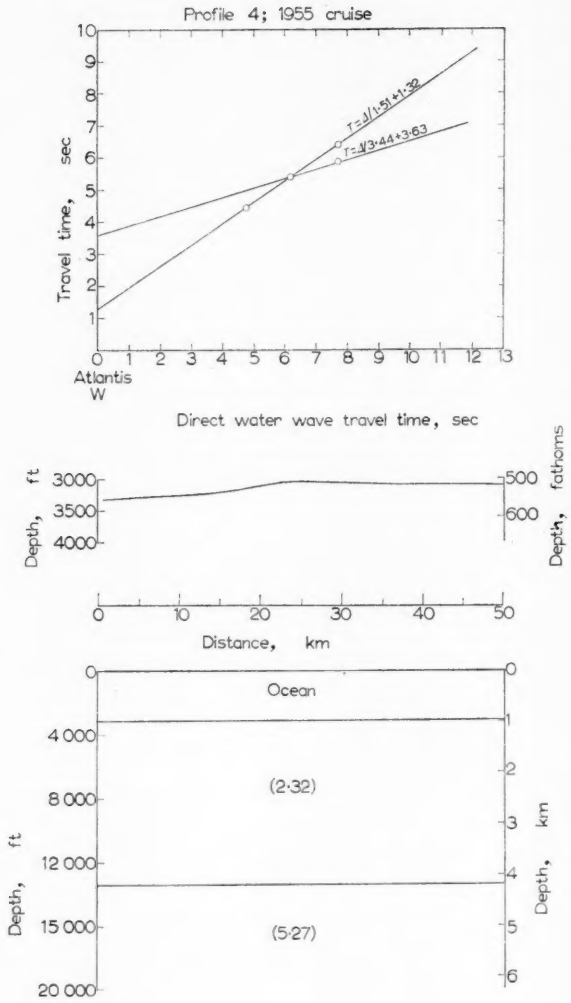
Profile 4; 1955 cruise
Travel time, sec
T=Δ/1·51+1·32
T=√3·44+3·63
Atlantis
W
Direct water wave travel time, sec
Depth, ft
Depth, fathoms
Distance, km
Ocean
(2·32)
(5·27)
Depth, ft
Depth, km

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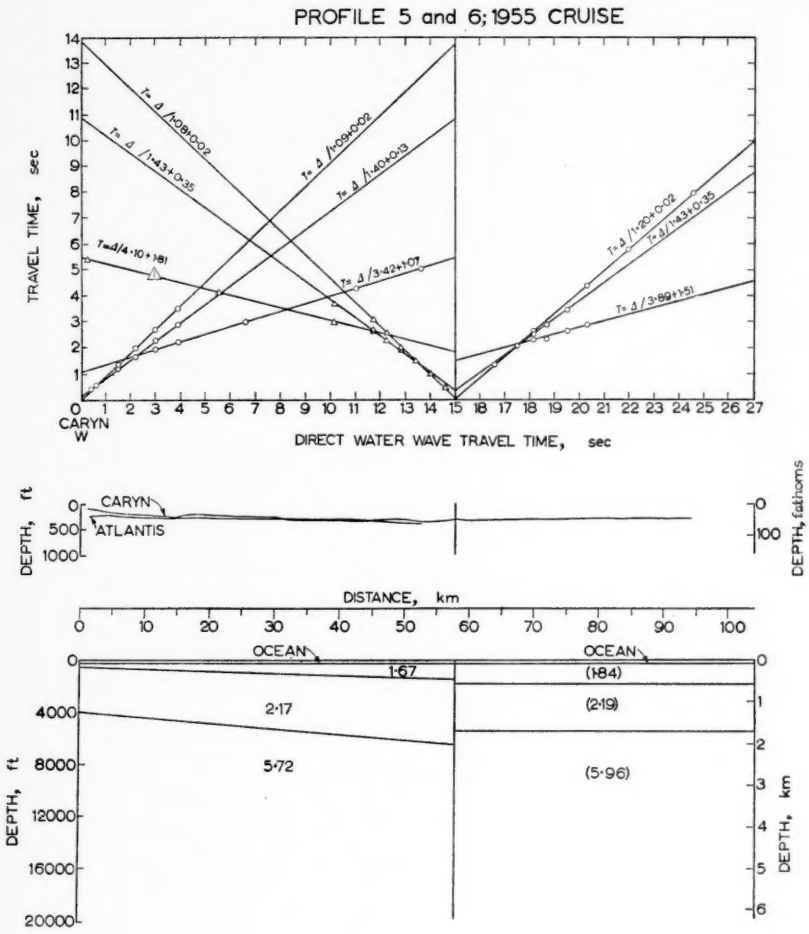
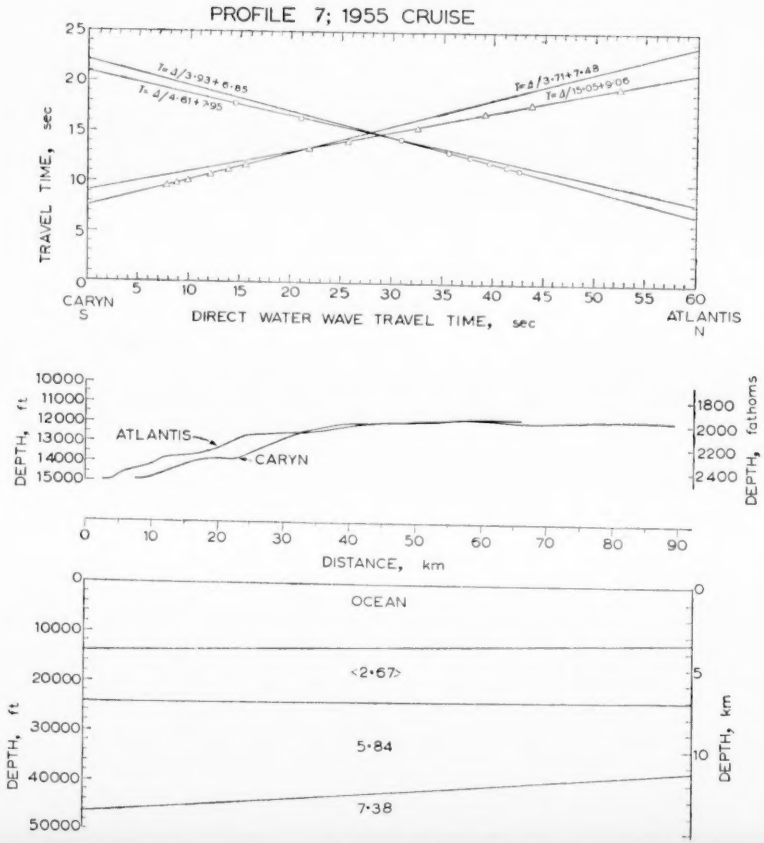
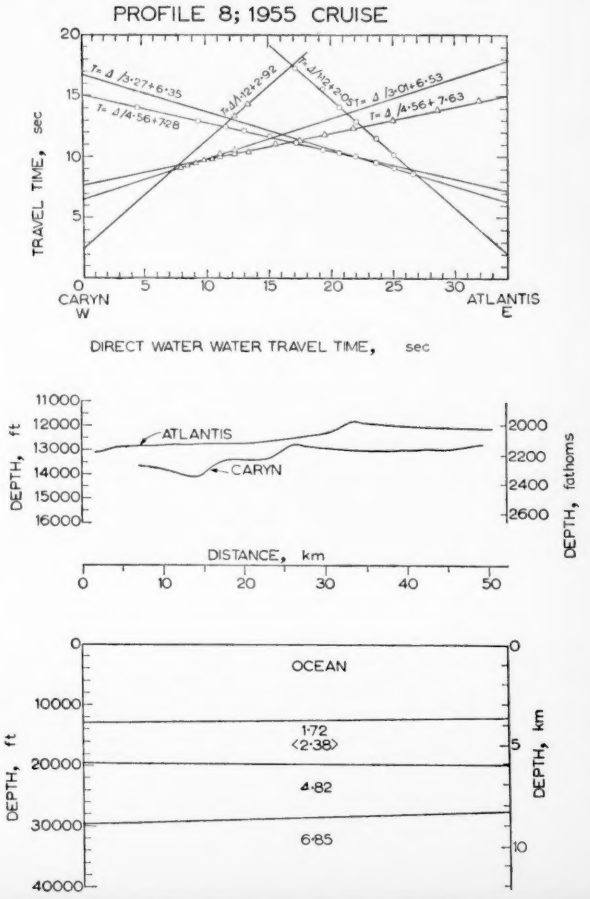

PROFILE 5 and 6; 1955 CRUISE
TRAVEL TIME, sec
DIRECT WATER WAVE TRAVEL TIME, sec
CARYN
W
T= Δ /1·09+0·02
T= Δ /1·43+0·35
T= Δ /1·09+0·02
T= Δ /1·40+0·13
T=Δ/4·10+1·81
T= Δ /3·42+1·07
T= Δ /1·20+0·02
T= Δ /1·43+0·35
T= Δ /3·89+1·51
DEPTH, ft
CARYN
ATLANTIS
DEPTH, fathoms
DISTANCE, km
OCEAN
OCEAN
1·67
2·17
5·72
(1·84)
(2·19)
(5·96)
DEPTH, ft
DEPTH, km


PROFILE 7; 1955 CRUISE
TRAVEL TIME, sec
T= Δ/3·93+6·85
T= Δ/4·61+7·95
T= Δ/3·71+7·48
T= Δ/15·05+9·06
CARYN
S
ATLANTIS
N
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
DEPTH, fathoms
ATLANTIS
CARYN
DISTANCE, km
OCEAN
<2·67>
5·84
7·38
DEPTH, km


PROFILE 8; 1955 CRUISE
TRAVEL TIME, sec
T= Δ/3·27+6·35
T= Δ/1·12+2·92
T= Δ/1·21+2·03
T= Δ/3·01+6·53
T= Δ/4·56+7·28
T= Δ/4·56+7·63
CARYN
W
ATLANTIS
E
DIRECT WATER WATER TRAVEL TIME, sec
DEPTH, ft
DEPTH, fathoms
ATLANTIS
CARYN
DISTANCE, km
OCEAN
1·72
<2·38>
4·82
6·85
DEPTH, km

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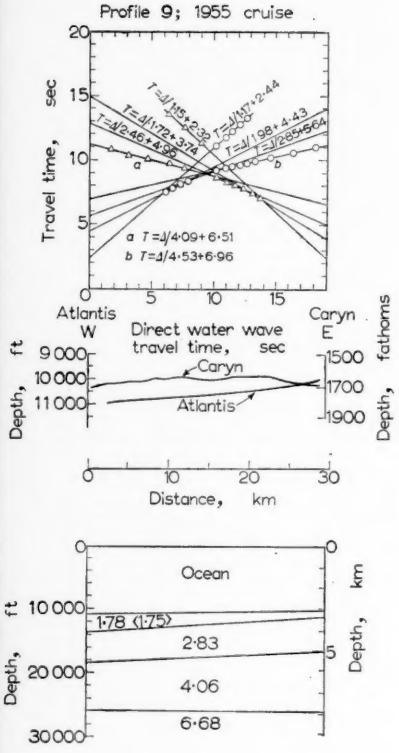
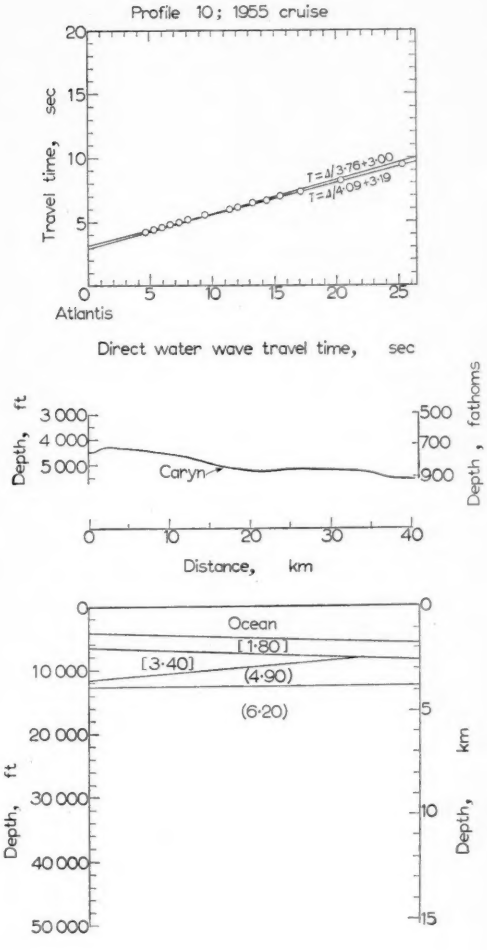
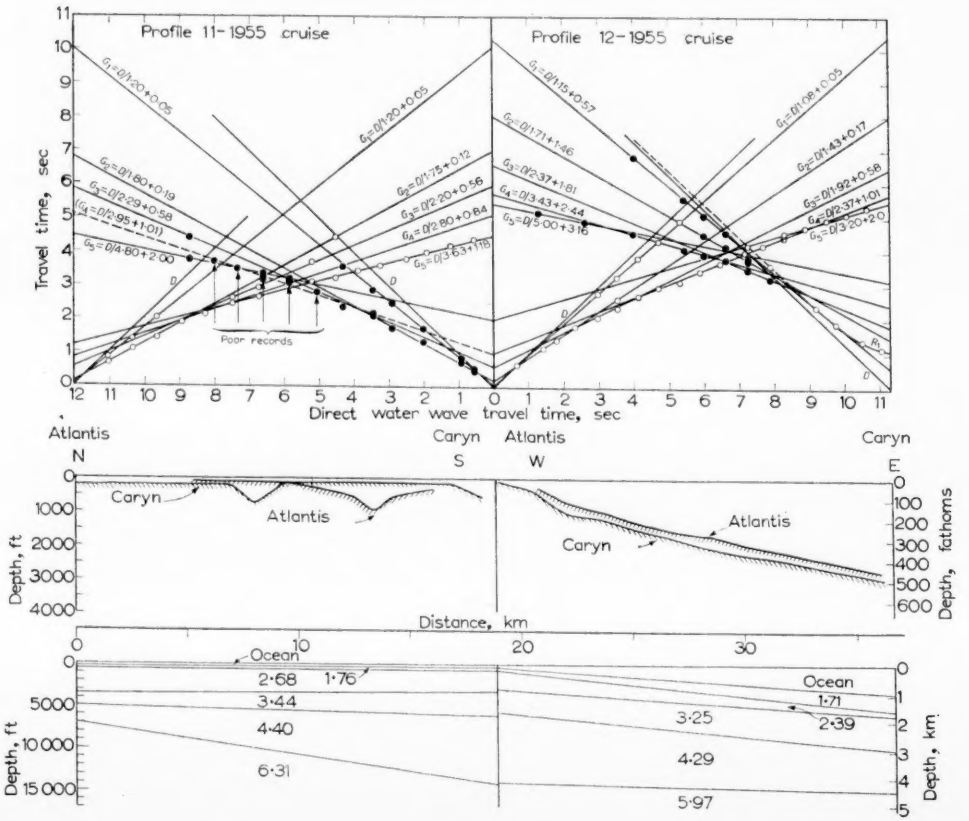

Profile 9; 1955 cruise
Travel time, sec
T=Δ/1·15+2·39
T=Δ/1·72+3·74
T=Δ/2·46+4·98
T=Δ/1·17+2·44
T=Δ/1·98+4·43
T=Δ/2·85+5·64
a T=Δ/4·09+6·51
b T=Δ/4·53+6·96
Atlantis W
Caryn E
Direct water wave travel time, sec
Depth, ft
Depth, fathoms
Caryn
Atlantis
Distance, km
Ocean
1·78 (1·75)
2·83
4·06
6·68
Depth, km


Profile 10; 1955 cruise
Travel time, sec
T=Δ/3·76+3·00
T=Δ/4·09+3·19
Atlantis
Direct water wave travel time, sec
Depth, ft
Caryn
Depth, fathoms
Distance, km
Ocean
[1·80]
[3·40]
(4·90)
(6·20)
Depth, km


Profile 11-1955 cruise
Profile 12-1955 cruise
Travel time, sec
Direct water wave travel time, sec
Poor records
Atlantis
Caryn
N
S
W
E
Depth, ft
Depth, fathoms
Distance, km
Ocean
2·68
1·76
3·44
4·40
6·31
1·71
2·39
3·25
4·29
5·97
Depth, km

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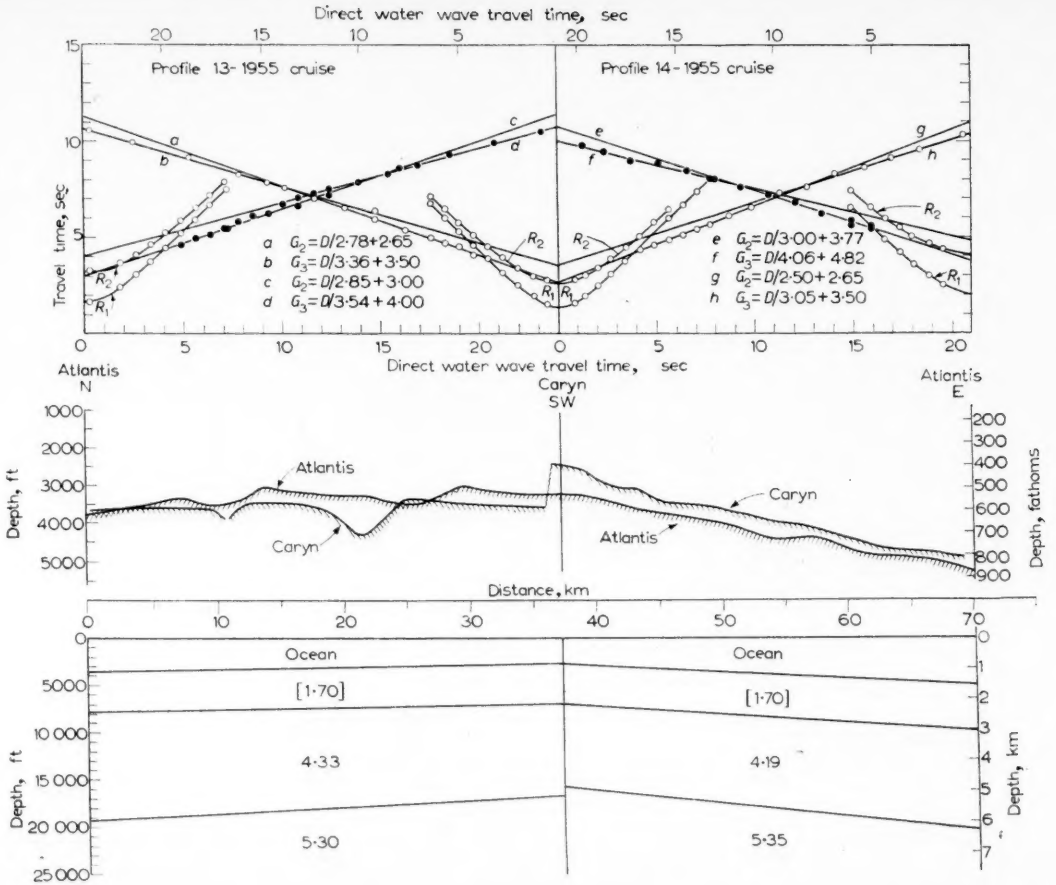
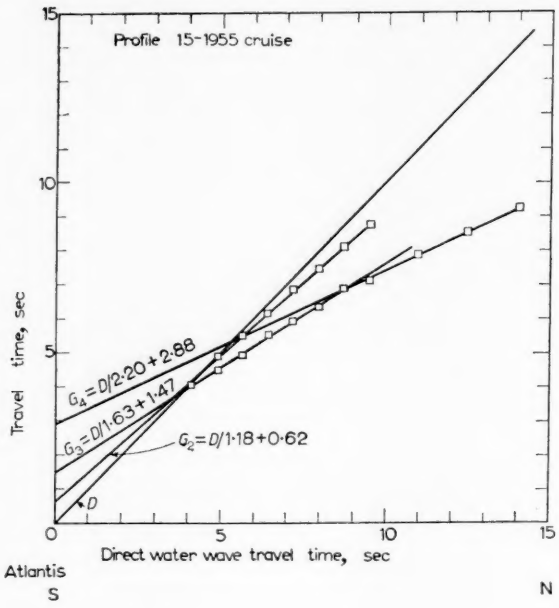
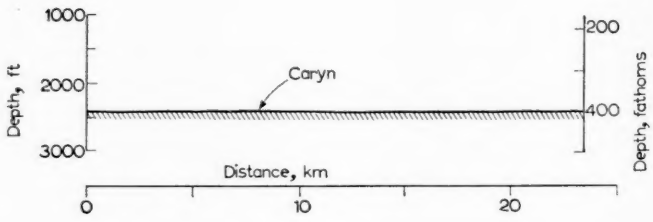
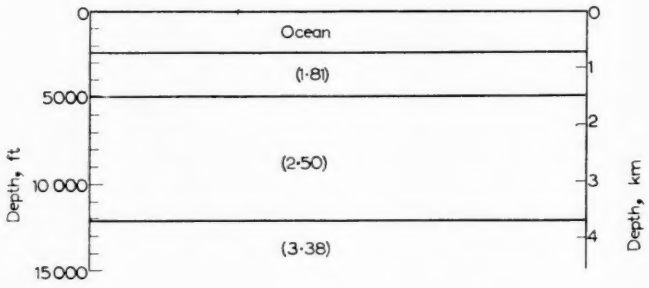
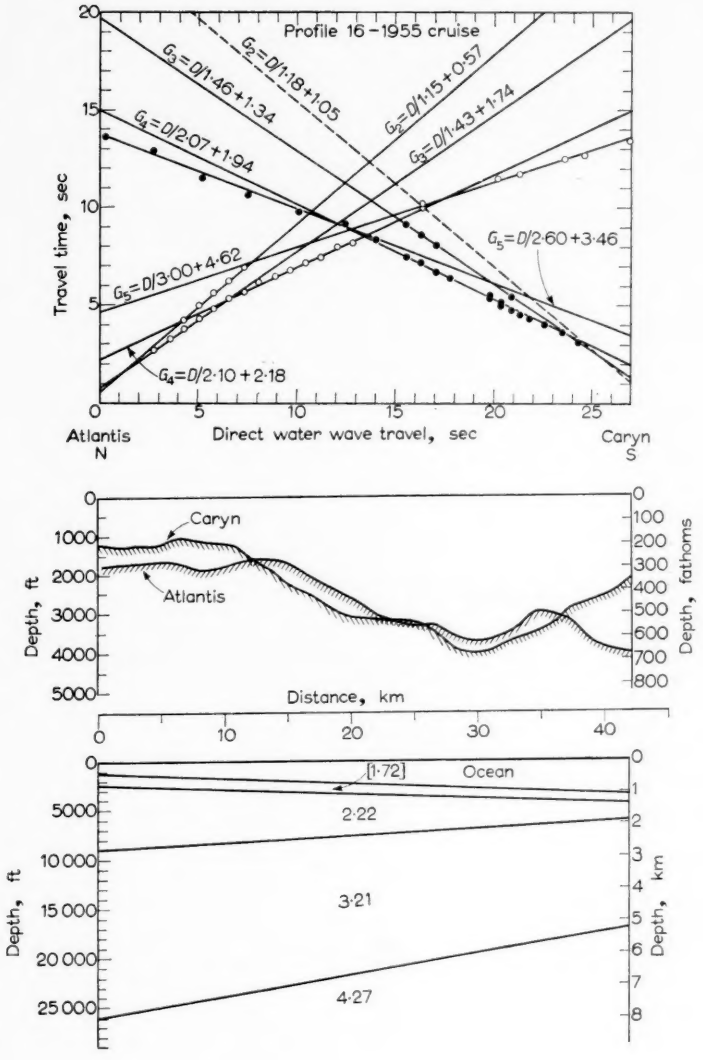
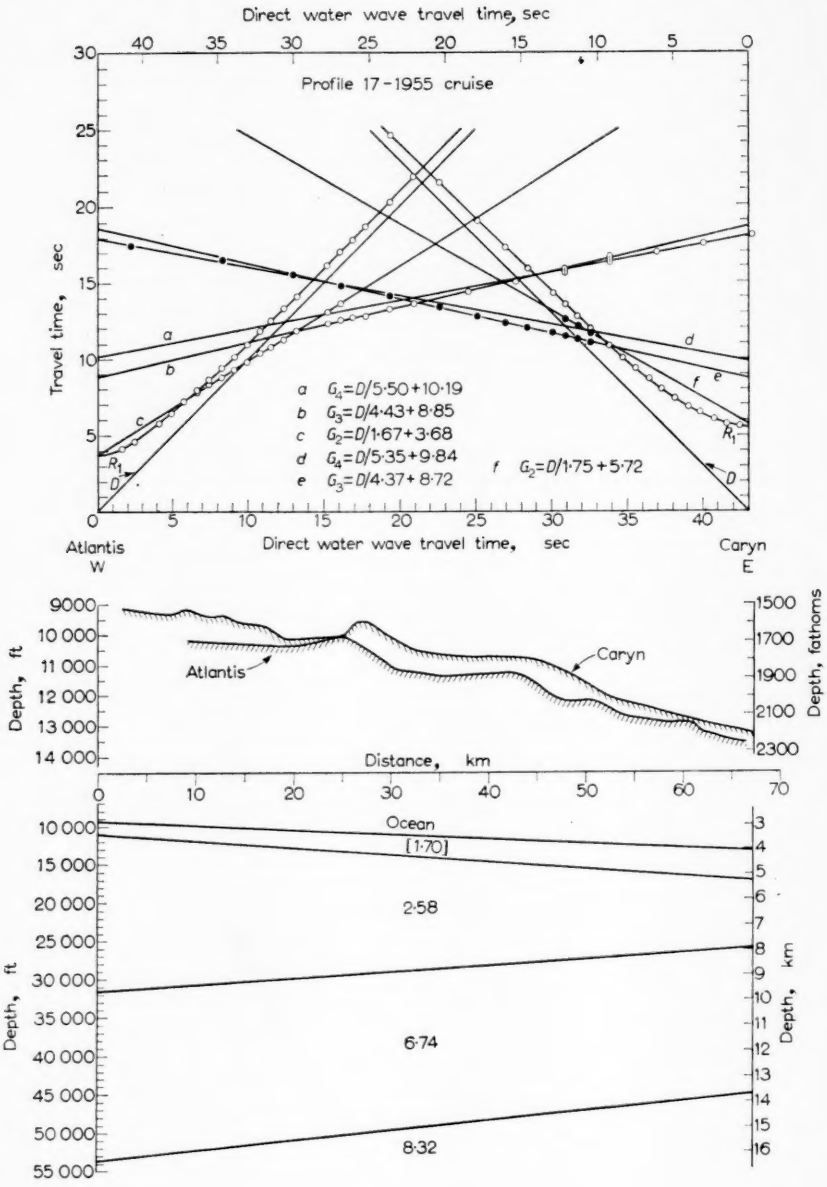

Direct water wave travel time, sec
Profile 13- 1955 cruise
Profile 14- 1955 cruise
Travel time, sec
a $G_2 = D/2{\cdot}78 + 2{\cdot}65$
b $G_3 = D/3{\cdot}36 + 3{\cdot}50$
c $G_2 = D/2{\cdot}85 + 3{\cdot}00$
d $G_3 = D/3{\cdot}54 + 4{\cdot}00$
e $G_2 = D/3{\cdot}00 + 3{\cdot}77$
f $G_3 = D/4{\cdot}06 + 4{\cdot}82$
g $G_2 = D/2{\cdot}50 + 2{\cdot}65$
h $G_3 = D/3{\cdot}05 + 3{\cdot}50$
Direct water wave travel time, sec
Atlantis N
Caryn SW
Atlantis E
Depth, ft
Depth, fathoms
Atlantis
Caryn
Caryn
Atlantis
Distance, km
Ocean
Ocean
[1·70]
[1·70]
4·33
4·19
5·30
5·35
Depth, ft
Depth, km

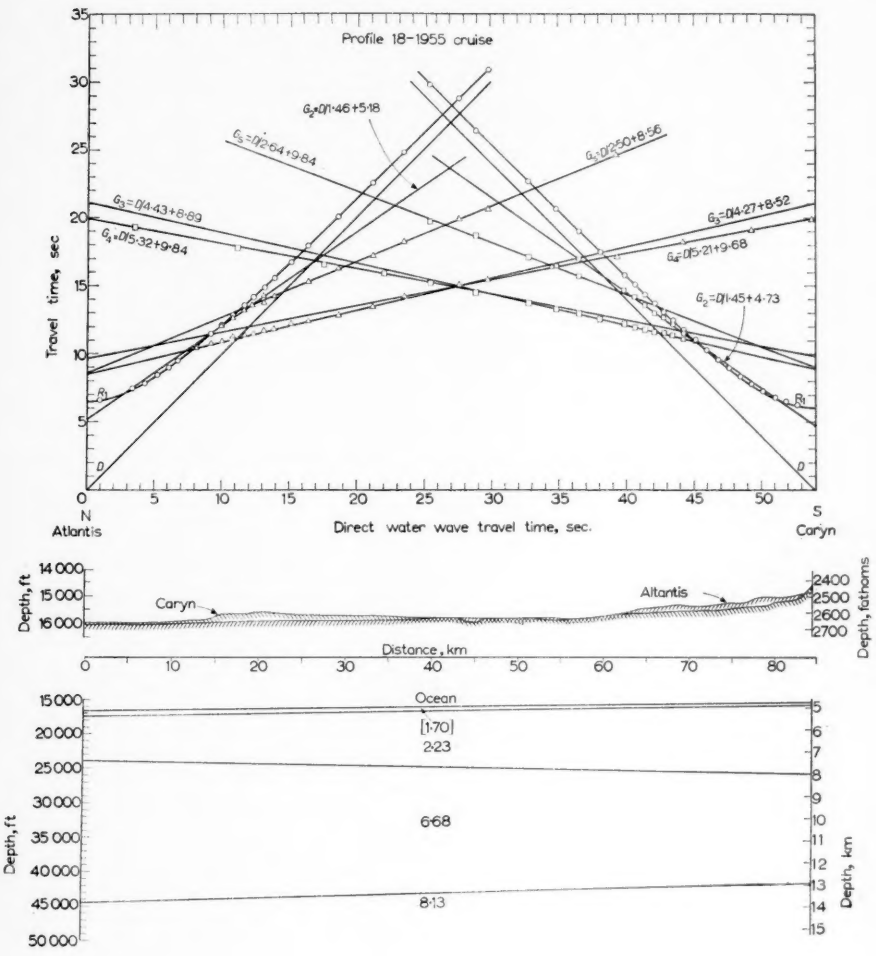

Profile 15-1955 cruise
Travel time, sec
$G_4 = D/2{\cdot}20 + 2{\cdot}88$
$G_3 = D/1{\cdot}63 + 1{\cdot}47$
$G_2 = D/1{\cdot}18 + 0{\cdot}62$
D
Direct water wave travel time, sec
Atlantis
S
N

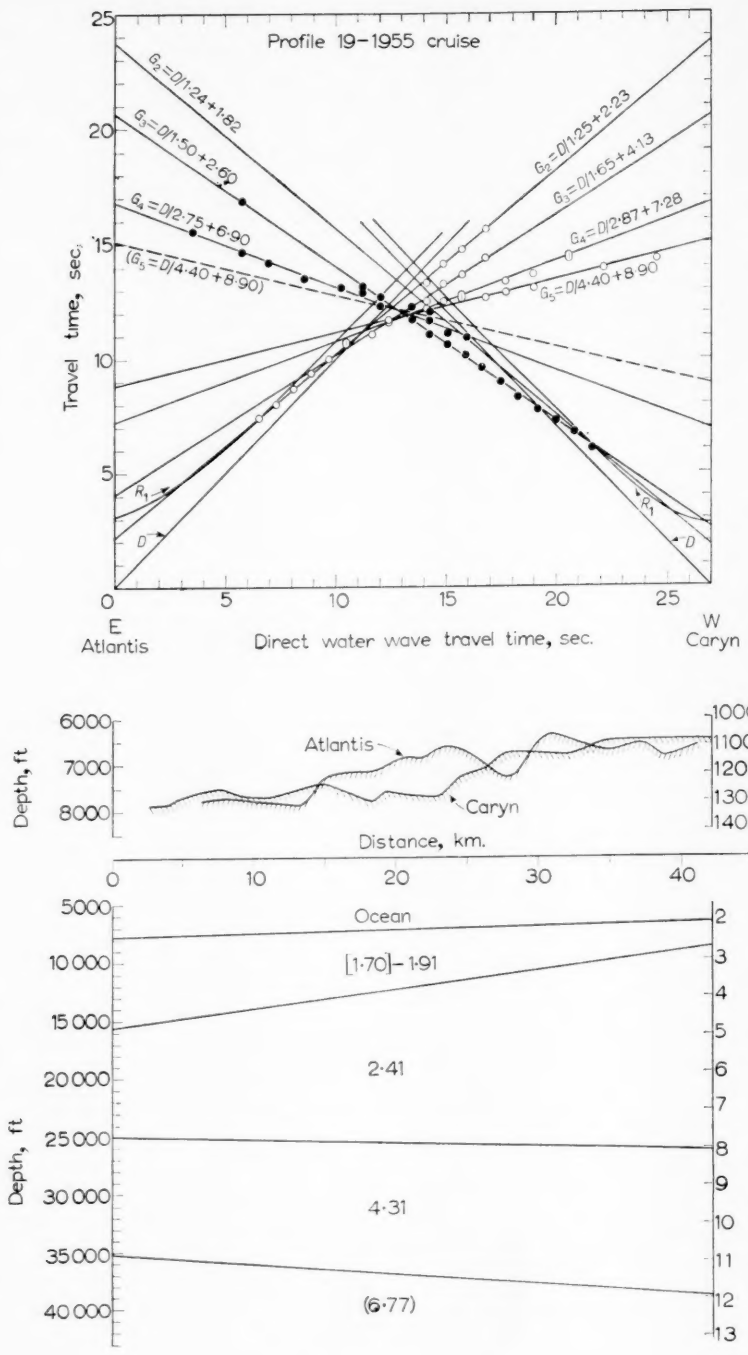

Depth, ft
Caryn
Depth, fathoms
Distance, km

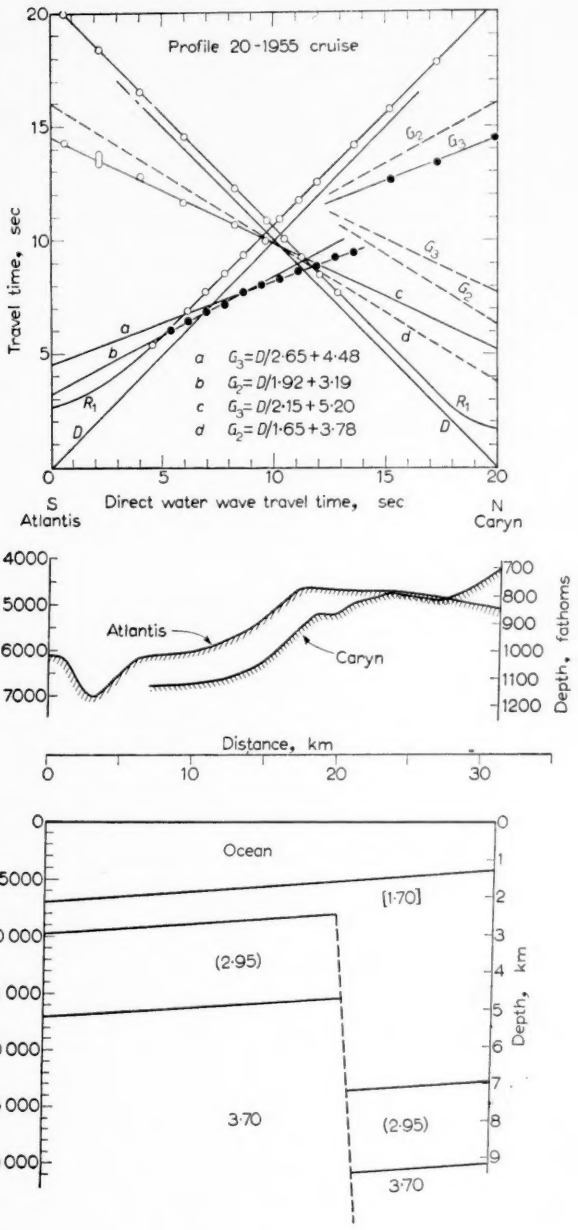

Ocean
(1·81)
(2·50)
(3·38)
Depth, ft
Depth, km


Profile 16 – 1955 cruise
$G_2=D/1{\cdot}18+1{\cdot}05$
$G_3=D/1{\cdot}46+1{\cdot}34$
$G_4=D/2{\cdot}07+1{\cdot}94$
$G_5=D/3{\cdot}00+4{\cdot}62$
$G_2=D/1{\cdot}15+0{\cdot}57$
$G_3=D/1{\cdot}43+1{\cdot}74$
$G_5=D/2{\cdot}60+3{\cdot}46$
$G_4=D/2{\cdot}10+2{\cdot}18$
Travel time, sec
Direct water wave travel, sec
Atlantis N
Caryn S
Caryn
Atlantis
Depth, ft
Depth, fathoms
Distance, km
[1·72]
Ocean
2·22
3·21
4·27
Depth, km


Direct water wave travel time, sec
Profile 17 - 1955 cruise
Travel time, sec
a $G_4 = D/5{\cdot}50 + 10{\cdot}19$
b $G_3 = D/4{\cdot}43 + 8{\cdot}85$
c $G_2 = D/1{\cdot}67 + 3{\cdot}68$
d $G_4 = D/5{\cdot}35 + 9{\cdot}84$
e $G_3 = D/4{\cdot}37 + 8{\cdot}72$
f $G_2 = D/1{\cdot}75 + 5{\cdot}72$
Atlantis W
Direct water wave travel time, sec
Caryn E
Depth, ft
Depth, fathoms
Atlantis
Caryn
Distance, km
Ocean
[1·70]
2·58
6·74
8·32
Depth, km


Profile 18–1955 cruise
G_2=0/1·46+5·18
G_5=0/2·64+9·84
G_3=0/4·43+8·89
G_4=0/5·32+9·84
G_3=0/2·50+8·56
G_3=0/4·27+8·52
G_4=0/5·21+9·68
G_2=0/1·45+4·73
R_1
R_2
D
Travel time, sec
N
Atlantis
Direct water wave travel time, sec.
S
Caryn
Depth, ft
Caryn
Atlantis
Depth, fathoms
Distance, km
Ocean
[1·70]
2·23
6·68
8·13
Depth, km


Profile 19–1955 cruise
$G_2 = D/1{\cdot}24 + 1{\cdot}82$
$G_3 = D/1{\cdot}50 + 2{\cdot}60$
$G_4 = D/2{\cdot}75 + 6{\cdot}90$
$(G_5 = D/4{\cdot}40 + 8{\cdot}90)$
$G_2 = D/1{\cdot}25 + 2{\cdot}23$
$G_3 = D/1{\cdot}65 + 4{\cdot}13$
$G_4 = D/2{\cdot}87 + 7{\cdot}28$
$G_5 = D/4{\cdot}40 + 8{\cdot}90$
Travel time, sec.
R_1
D
E
Atlantis
Direct water wave travel time, sec.
W
Caryn
Depth, ft
Depth, fathoms
Atlantis
Caryn
Distance, km.
Ocean
[1·70]– 1·91
2·41
4·31
(6·77)
Depth, km


Profile 20-1955 cruise
Travel time, sec
Direct water wave travel time, sec
S Atlantis
N Caryn
a $G_3 = D/2{\cdot}65 + 4{\cdot}48$
b $G_2 = D/1{\cdot}92 + 3{\cdot}19$
c $G_3 = D/2{\cdot}15 + 5{\cdot}20$
d $G_2 = D/1{\cdot}65 + 3{\cdot}78$
Depth, ft
Depth, fathoms
Atlantis
Caryn
Distance, km
Ocean
[1·70]
(2·95)
3·70
(2·95)
3·70
Depth, ft
Depth, km

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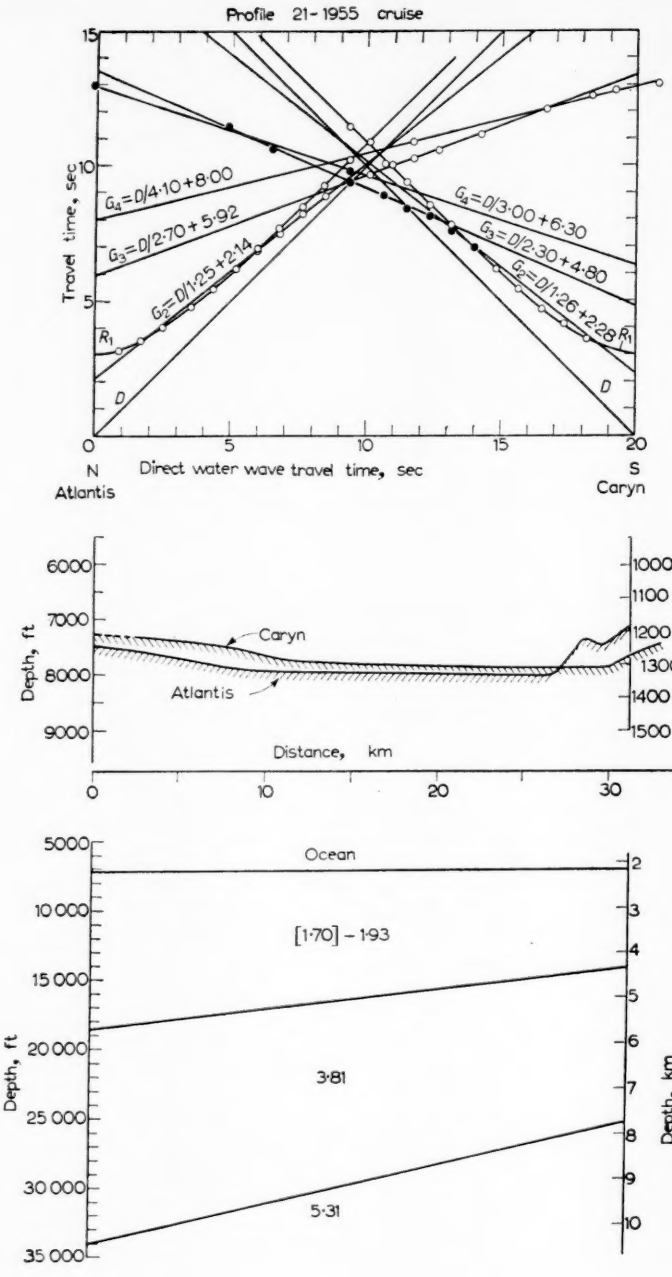
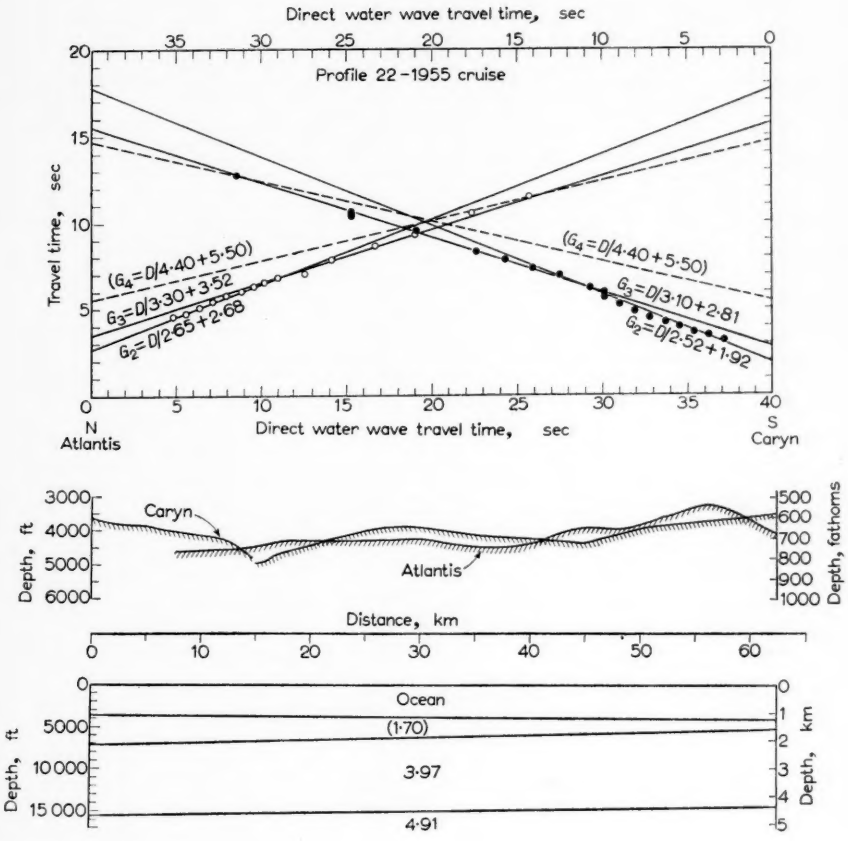
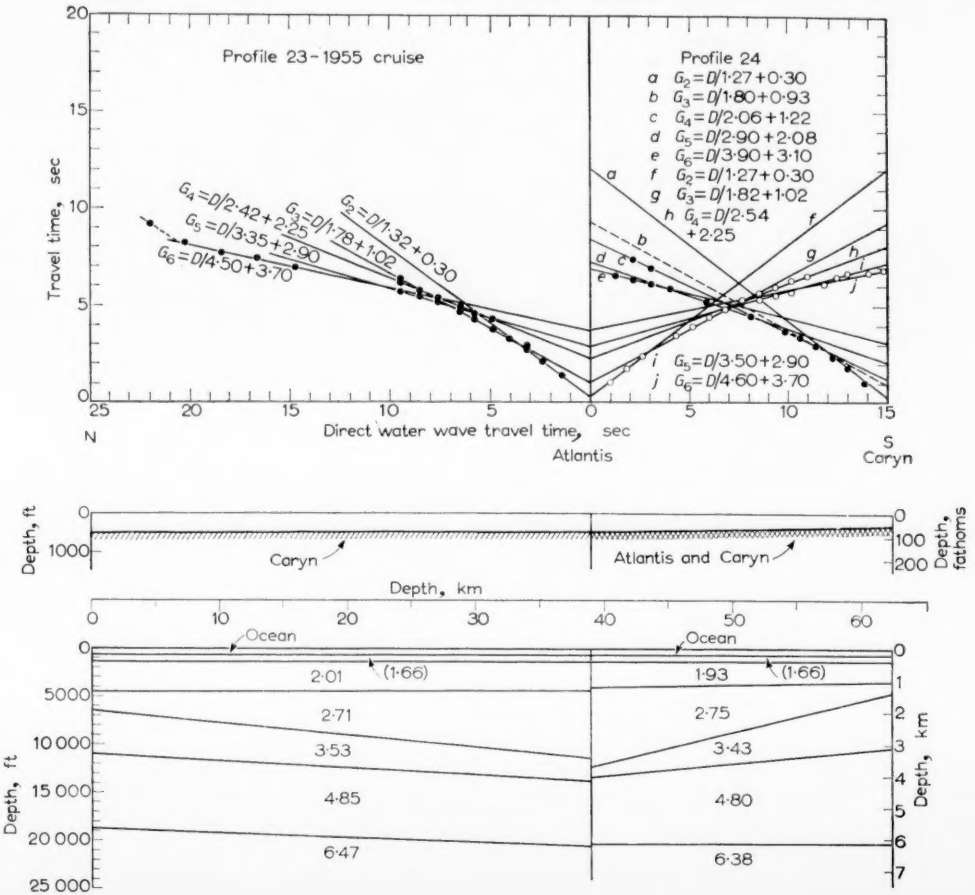

Profile 21-1955 cruise
Travel time, sec
Direct water wave travel time, sec
N
Atlantis
S
Caryn
$G_4 = D/4{\cdot}10 + 8{\cdot}00$
$G_3 = D/2{\cdot}70 + 5{\cdot}92$
$G_2 = D/1{\cdot}25 + 2{\cdot}14$
$G_4 = D/3{\cdot}00 + 6{\cdot}30$
$G_3 = D/2{\cdot}30 + 4{\cdot}80$
$G_2 = D/1{\cdot}26 + 2{\cdot}28$
R_1
D
Depth, ft
Depth, fathoms
Caryn
Atlantis
Distance, km
Ocean
[1·70] – 1·93
3·81
5·31
Depth, km


Direct water wave travel time, sec
Profile 22–1955 cruise
Travel time, sec
$(G_4 = D/4{\cdot}40 + 5{\cdot}50)$
$G_3 = D/3{\cdot}30 + 3{\cdot}52$
$G_2 = D/2{\cdot}65 + 2{\cdot}68$
$(G_4 = D/4{\cdot}40 + 5{\cdot}50)$
$G_3 = D/3{\cdot}10 + 2{\cdot}81$
$G_2 = D/2{\cdot}52 + 1{\cdot}92$
N
Atlantis
Direct water wave travel time, sec
S
Caryn
Depth, ft
Caryn
Atlantis
Depth, fathoms
Distance, km
Ocean
(1·70)
3·97
4·91
Depth, ft
Depth, km


Profile 23 - 1955 cruise
Profile 24
a $G_2 = D/1{\cdot}27 + 0{\cdot}30$
b $G_3 = D/1{\cdot}80 + 0{\cdot}93$
c $G_4 = D/2{\cdot}06 + 1{\cdot}22$
d $G_5 = D/2{\cdot}90 + 2{\cdot}08$
e $G_6 = D/3{\cdot}90 + 3{\cdot}10$
f $G_2 = D/1{\cdot}27 + 0{\cdot}30$
g $G_3 = D/1{\cdot}82 + 1{\cdot}02$
h $G_4 = D/2{\cdot}54 + 2{\cdot}25$
i $G_5 = D/3{\cdot}50 + 2{\cdot}90$
j $G_6 = D/4{\cdot}60 + 3{\cdot}70$
$G_4 = D/2{\cdot}42 + 2{\cdot}25$
$G_3 = D/1{\cdot}78 + 1{\cdot}02$
$G_2 = D/1{\cdot}32 + 0{\cdot}30$
$G_5 = D/3{\cdot}35 + 2{\cdot}90$
$G_6 = D/4{\cdot}50 + 3{\cdot}70$
Travel time, sec
Direct water wave travel time, sec
N
Atlantis
S
Caryn
Depth, ft
Caryn
Atlantis and Caryn
Depth, fathoms
Depth, km
Ocean
Ocean
2·01
(1·66)
1·93
(1·66)
2·71
2·75
3·53
3·43
4·85
4·80
6·47
6·38
Depth, ft
Depth, km

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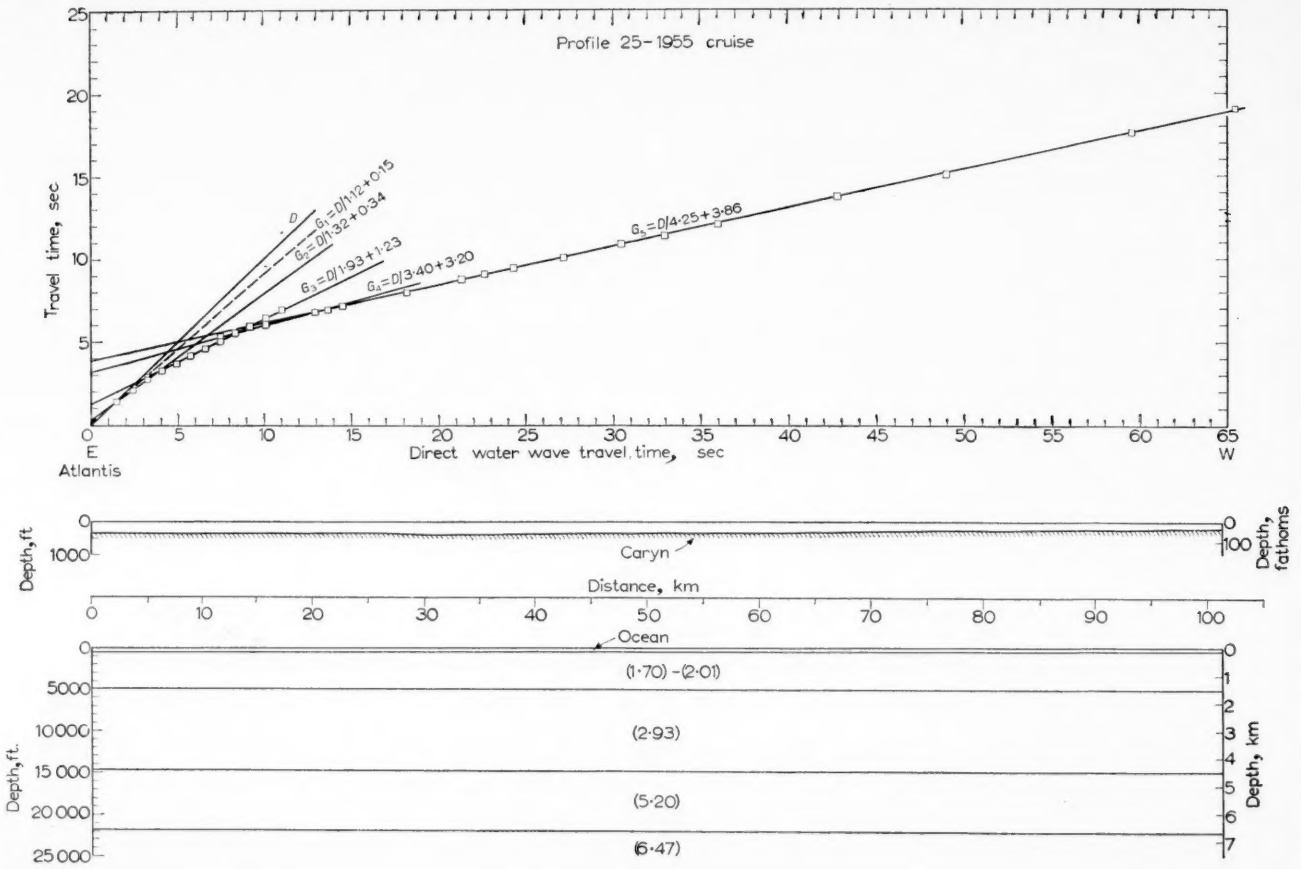
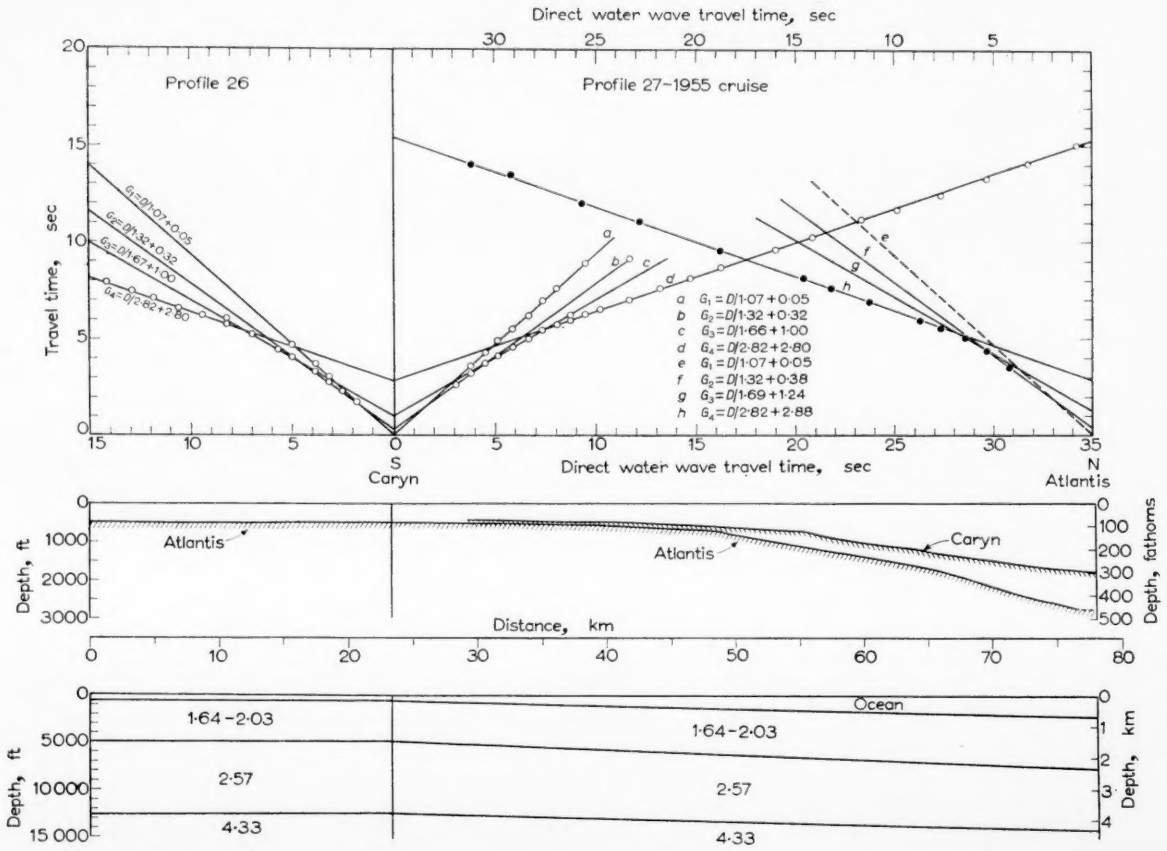

Profile 25-1955 cruise
Travel time, sec
Direct water wave travel time, sec
E
W
Atlantis
D
G1=D/1·12+0·15
G2=D/1·32+0·34
G3=D/1·93+1·23
G4=D/3·40+3·20
G5=D/4·25+3·86
Caryn
Distance, km
Ocean
Depth, ft
Depth, fathoms
Depth, km
(1·70) -(2·01)
(2·93)
(5·20)
(6·47)


Direct water wave travel time, sec
Profile 26
Profile 27–1955 cruise
Travel time, sec
$G_1 = D/1{\cdot}07 + 0{\cdot}05$
$G_2 = D/1{\cdot}32 + 0{\cdot}32$
$G_3 = D/1{\cdot}67 + 1{\cdot}00$
$G_4 = D/2{\cdot}82 + 2{\cdot}80$
a $G_1 = D/1{\cdot}07 + 0{\cdot}05$
b $G_2 = D/1{\cdot}32 + 0{\cdot}32$
c $G_3 = D/1{\cdot}66 + 1{\cdot}00$
d $G_4 = D/2{\cdot}82 + 2{\cdot}80$
e $G_1 = D/1{\cdot}07 + 0{\cdot}05$
f $G_2 = D/1{\cdot}32 + 0{\cdot}38$
g $G_3 = D/1{\cdot}69 + 1{\cdot}24$
h $G_4 = D/2{\cdot}82 + 2{\cdot}88$
S
Caryn
Direct water wave travel time, sec
N
Atlantis
Depth, ft
Atlantis
Atlantis
Caryn
Depth, fathoms
Distance, km
Ocean
1·64 – 2·03
2·57
4·33
1·64 – 2·03
2·57
4·33
Depth, ft
Depth, km

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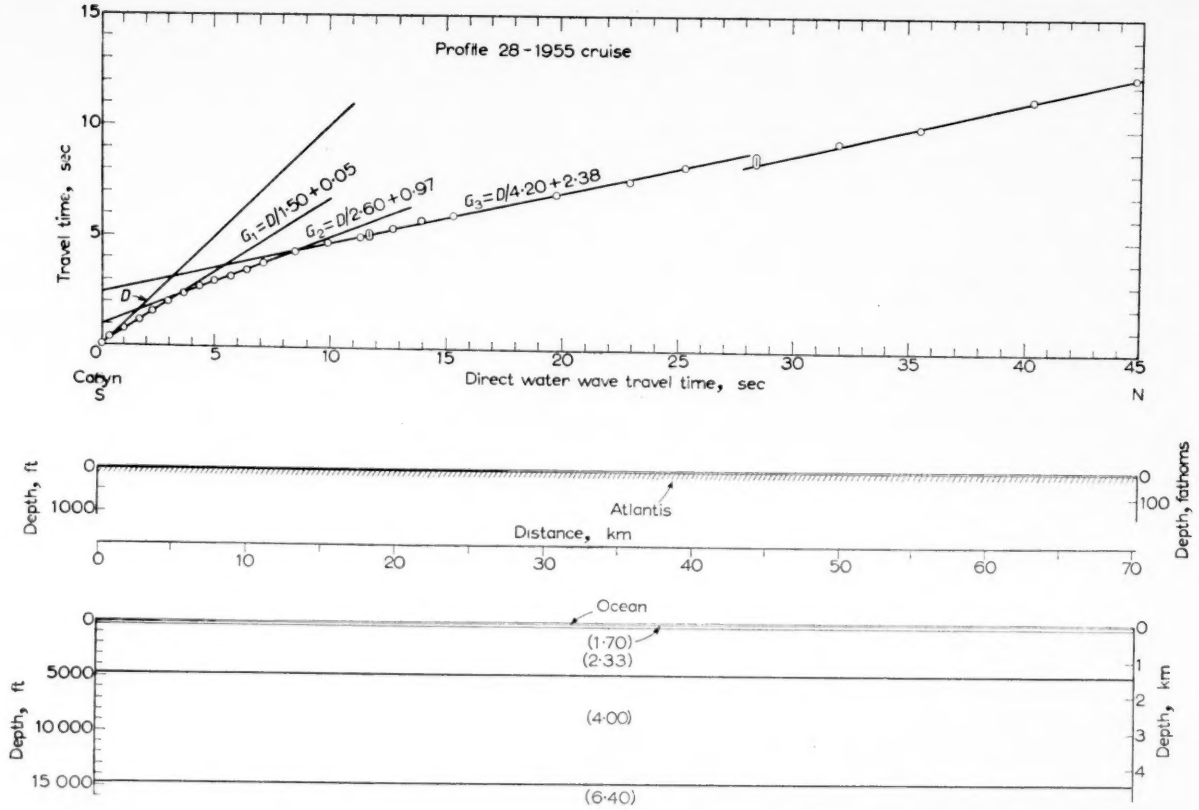
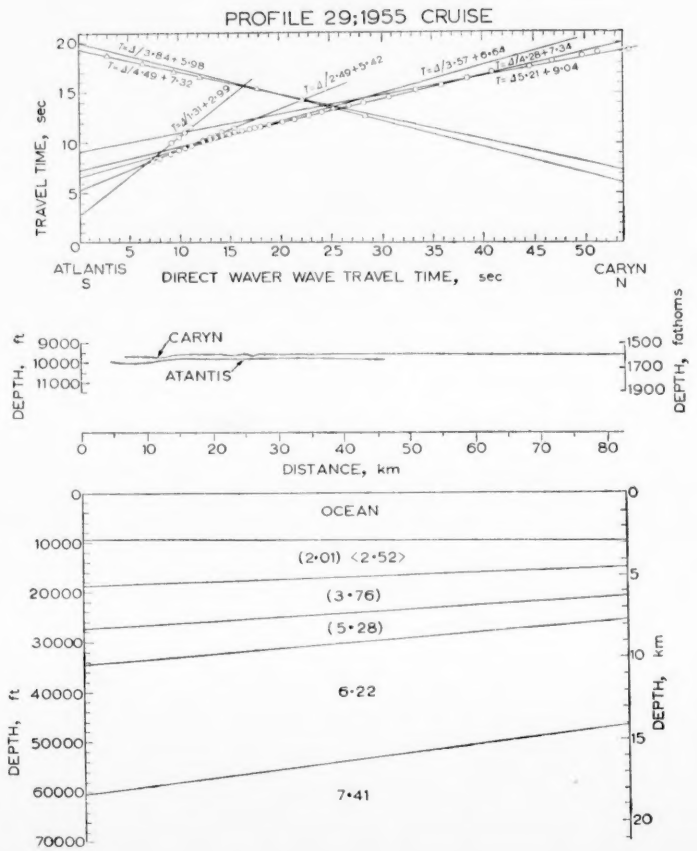
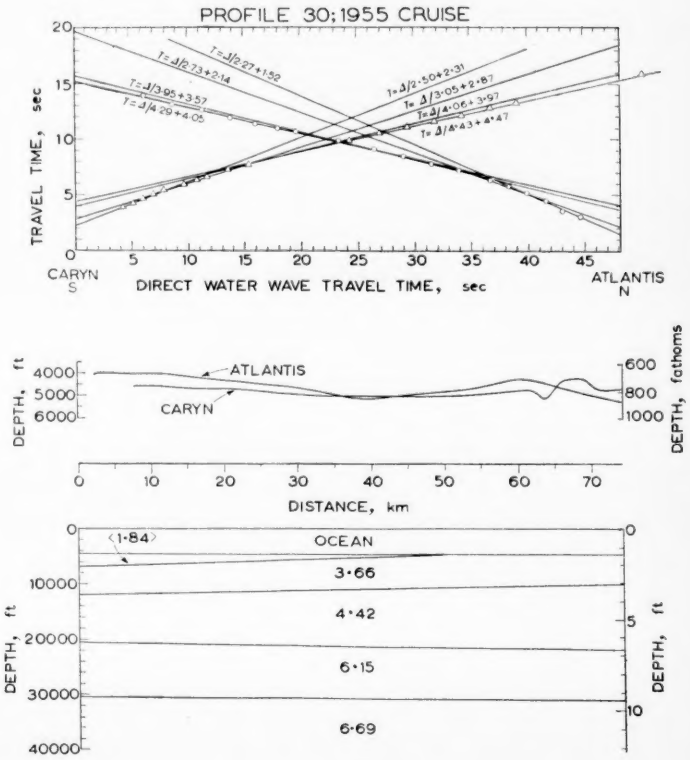

Profile 28 - 1955 cruise
Travel time, sec
Direct water wave travel time, sec
$G_1 = D/1{\cdot}50 + 0{\cdot}05$
$G_2 = D/2{\cdot}60 + 0{\cdot}97$
$G_3 = D/4{\cdot}20 + 2{\cdot}38$
D
Coryn
S
N
Depth, ft
Depth, fathoms
Atlantis
Distance, km
Ocean
(1·70)
(2·33)
(4·00)
(6·40)
Depth, km


PROFILE 29;1955 CRUISE
TRAVEL TIME, sec
DIRECT WAVER WAVE TRAVEL TIME, sec
ATLANTIS S
CARYN N
T=Δ/3·84+5·98
T=Δ/4·49+7·32
T=Δ/2·49+5·42
T=Δ/1·31+2·99
T=Δ/3·57+6·64
T=Δ/4·28+7·34
T=Δ5·21+9·04
CARYN
ATANTIS
DEPTH, ft
DEPTH, fathoms
DISTANCE, km
OCEAN
(2·01) ⟨2·52⟩
(3·76)
(5·28)
6·22
7·41
DEPTH, km


PROFILE 30;1955 CRUISE
TRAVEL TIME, sec
DIRECT WATER WAVE TRAVEL TIME, sec
CARYN S
ATLANTIS N
T=Δ/2·73+2·14
T=Δ/3·95+3·57
T=Δ/4·29+4·05
T=Δ/2·27+1·52
T=Δ/2·50+2·31
T=Δ/3·05+2·87
T=Δ/4·06+3·97
T=Δ/4·43+4·47
ATLANTIS
CARYN
DEPTH, ft
DEPTH, fathoms
DISTANCE, km
⟨1·84⟩
OCEAN
3·66
4·42
6·15
6·69

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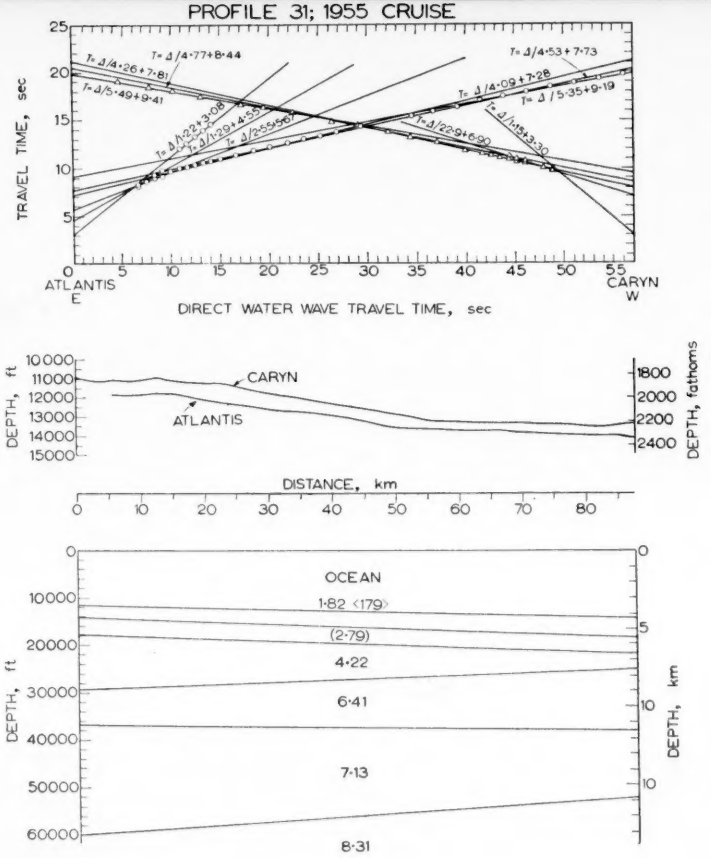
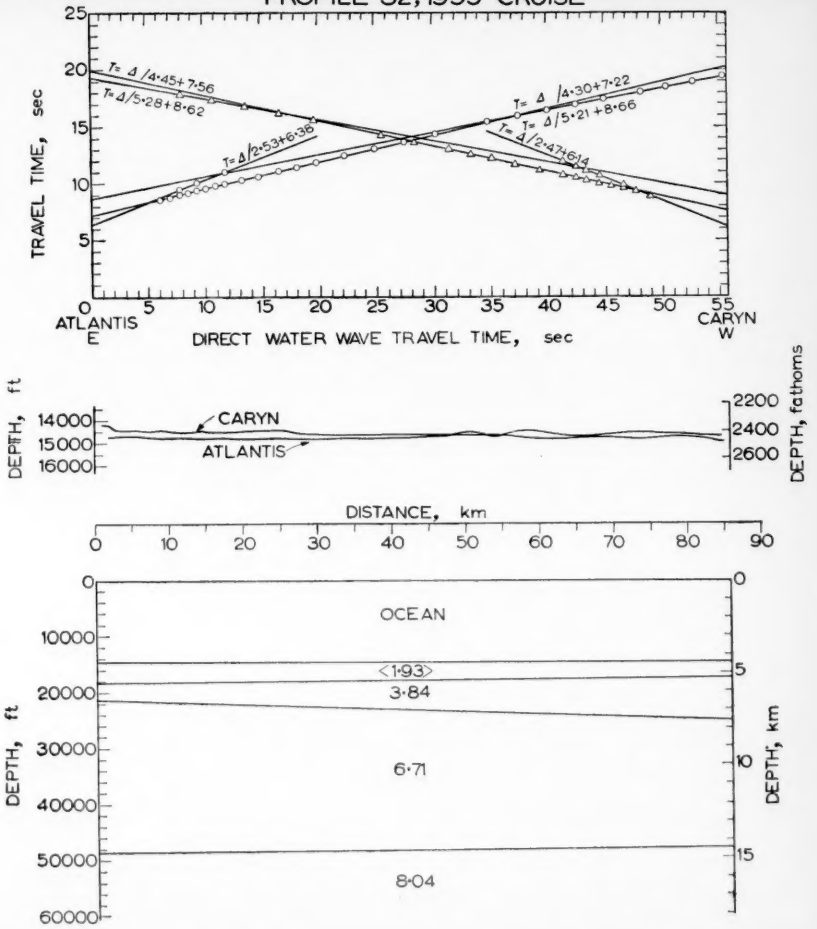
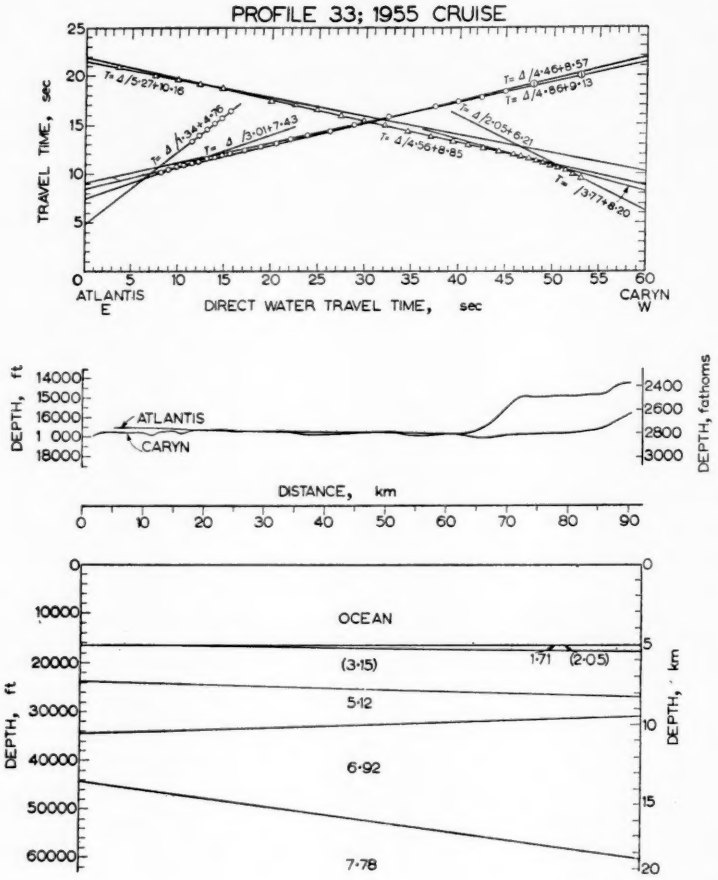
PROFILE 31; 1955 CRUISE



PROFILE 32; 1955 CRUISE




PROFILE 33; 1955 CRUISE
TRAVEL TIME, sec
DIRECT WATER TRAVEL TIME, sec
ATLANTIS E
CARYN W
T= Δ/5·27+10·16
T= Δ/4·46+8·57
T= Δ/4·86+9·13
T= Δ/4·56+8·85
T= Δ/3·01+7·43
T= Δ/3·77+8·20
DEPTH, ft
DEPTH, fathoms
ATLANTIS
CARYN
DISTANCE, km
OCEAN
(3·15)
1·71
(2·05)
5·12
6·92
7·78
DEPTH, km

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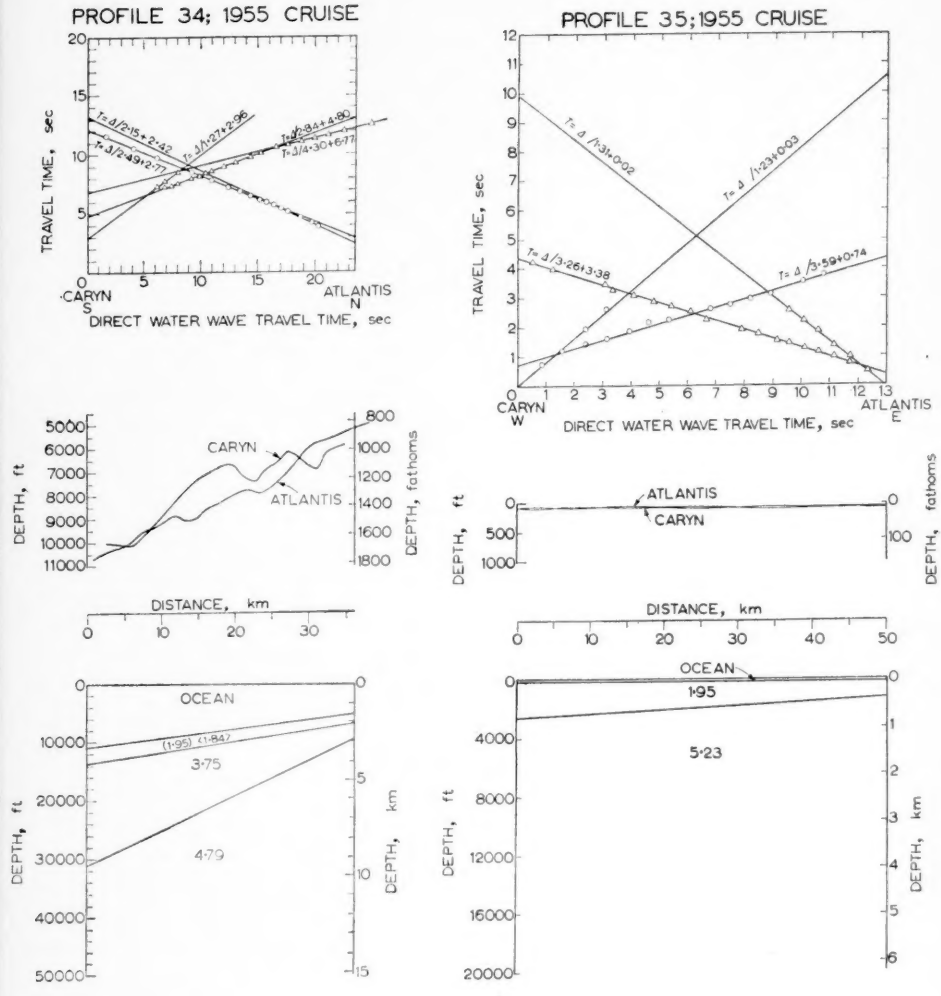
PROFILE 34; 1955 CRUISE
TRAVEL TIME, sec
T= Δ/2·15+2·42
T= Δ/1·27+2·96
T= Δ/2·49+2·77
T= Δ/2·34+4·80
T= Δ/4·30+6·77
CARYN
S
ATLANTIS
N
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
DEPTH, fathoms
CARYN
ATLANTIS
DISTANCE, km
OCEAN
(1·95) (1·84?)
3·75
4·79
DEPTH, km
PROFILE 35;1955 CRUISE
TRAVEL TIME, sec
T= Δ /h3i·002
T= Δ /1·23+0·03
T= Δ/3·26+3·38
T= Δ /3·59+0·74
CARYN
W
ATLANTIS
E
DIRECT WATER WAVE TRAVEL TIME, sec
ATLANTIS
CARYN
DISTANCE, km
OCEAN
1·95
5·23

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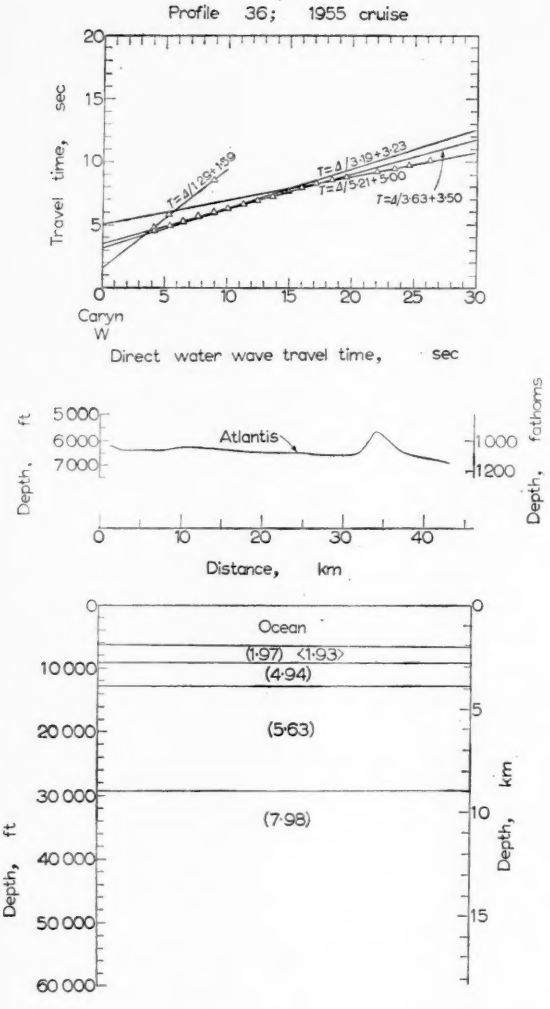
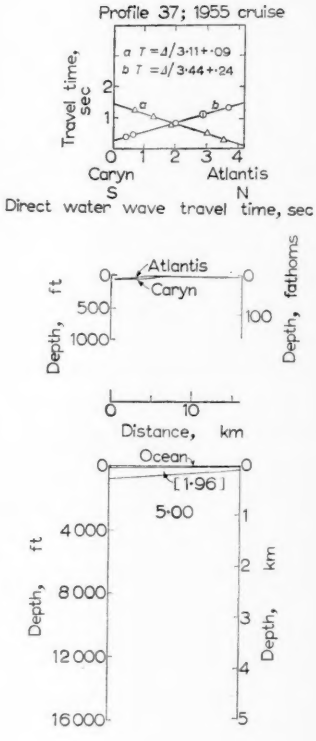
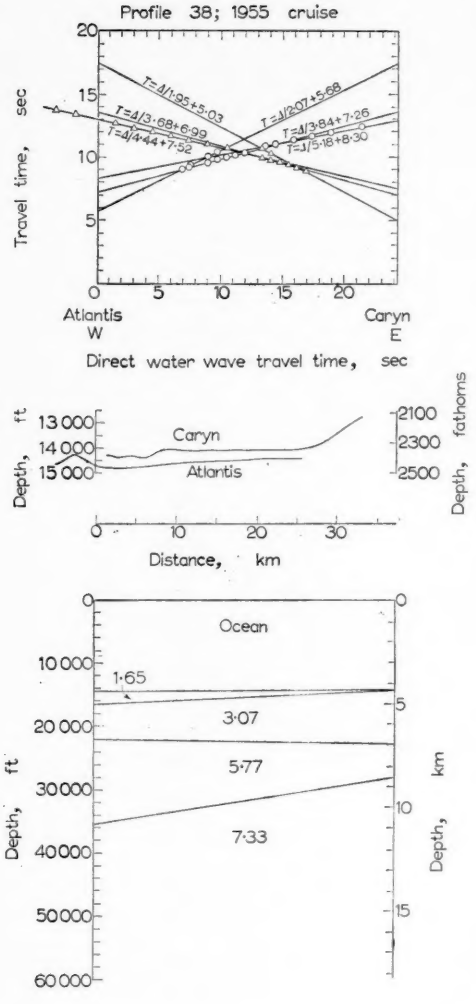
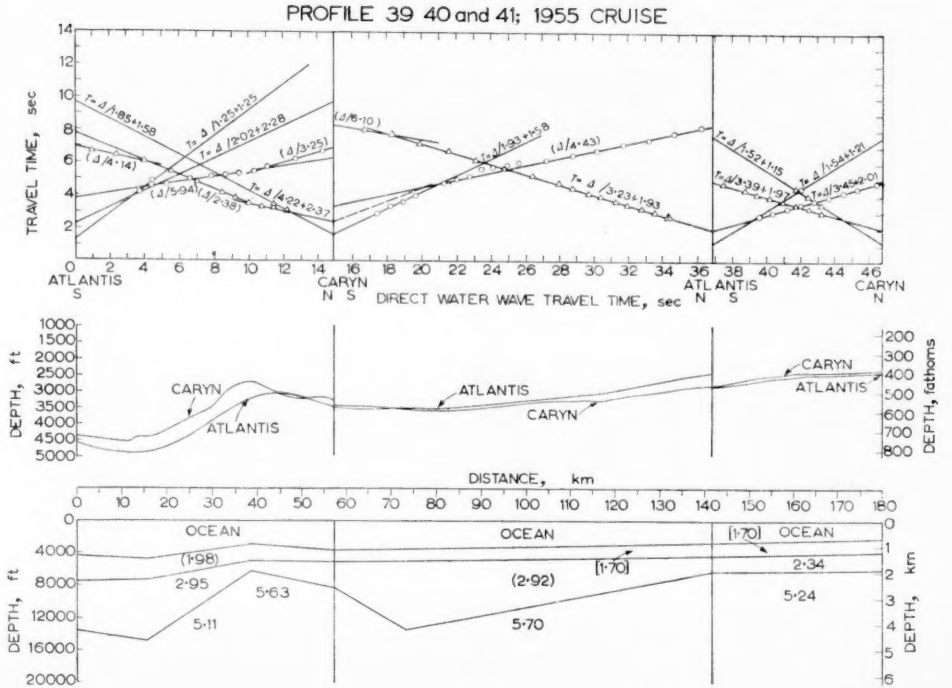

Profile 36; 1955 cruise
Travel time, sec
T=Δ/1·29+1·59
T=Δ/3·19+3·23
T=Δ/5·21+5·00
T=Δ/3·63+3·50
Caryn
W
Direct water wave travel time, sec
Depth, ft
Atlantis
Depth, fathoms
Distance, km
Ocean
(1·97) <1·93>
(4·94)
(5·63)
(7·98)
Depth, km


Profile 37; 1955 cruise
a T=Δ/3·11+·09
b T=Δ/3·44+·24
Travel time, sec
Caryn
S
Atlantis
N
Direct water wave travel time, sec
Depth, ft
Atlantis
Caryn
Depth, fathoms
Distance, km
Ocean
[1·96]
5·00
Depth, km


Profile 38; 1955 cruise
Travel time, sec
T=Δ/1·95+5·03
T=Δ/3·68+6·99
T=Δ/4·44+7·52
T=Δ/2·07+5·68
T=Δ/3·84+7·26
T=Δ/5·18+8·30
Atlantis
W
Caryn
E
Direct water wave travel time, sec
Depth, ft
Depth, fathoms
Caryn
Atlantis
Distance, km
Ocean
1·65
3·07
5·77
7·33
Depth, ft
Depth, km


PROFILE 39 40 and 41; 1955 CRUISE
TRAVEL TIME, sec
DIRECT WATER WAVE TRAVEL TIME, sec
ATLANTIS S
CARYN N S
ATLANTIS N S
CARYN N
DEPTH, ft
DEPTH, fathoms
CARYN
ATLANTIS
DISTANCE, km
OCEAN
(1·98)
2·95
5·11
5·63
(2·92)
5·70
[1·70]
2·34
5·24
DEPTH, km

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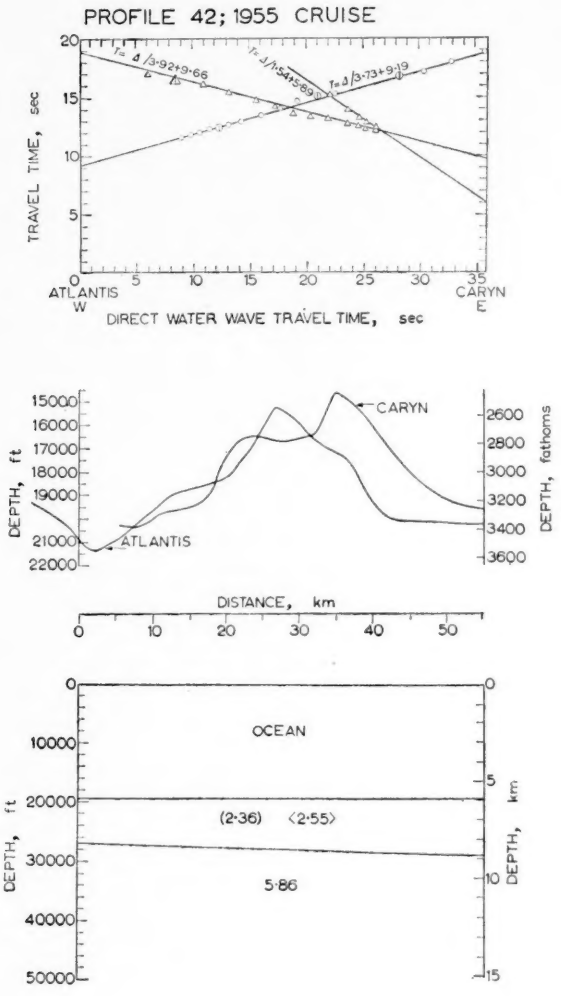
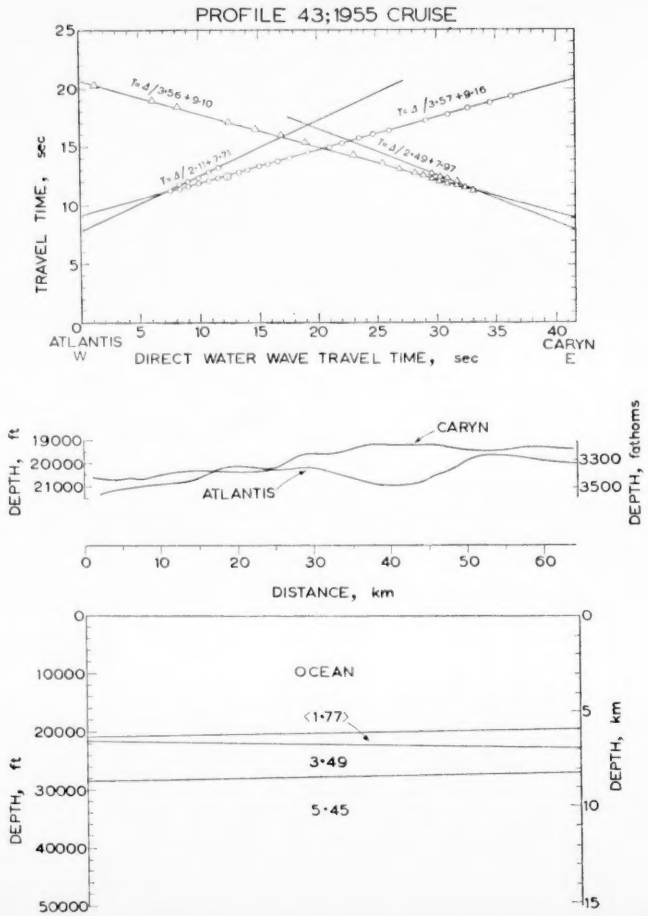
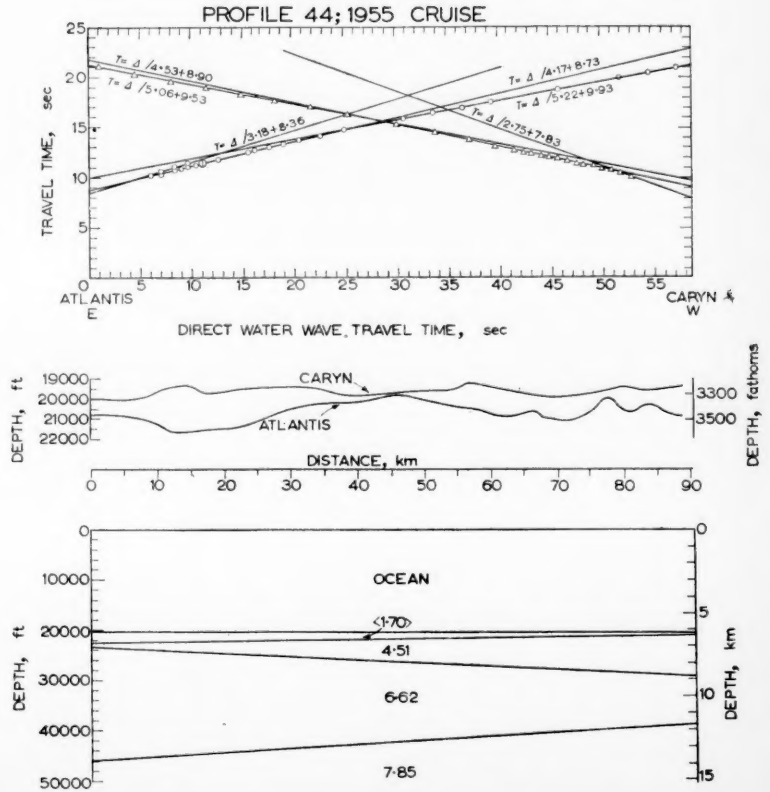

PROFILE 42; 1955 CRUISE
TRAVEL TIME, sec
DIRECT WATER WAVE TRAVEL TIME, sec
ATLANTIS
W
CARYN
E
DEPTH, ft
DEPTH, fathoms
CARYN
ATLANTIS
DISTANCE, km
OCEAN
(2·36)
⟨2·55⟩
5·86
DEPTH, km


PROFILE 43; 1955 CRUISE
TRAVEL TIME, sec
T= Δ /3·56 + 9·10
T= Δ /3·57 + 9·16
T= Δ /2·11 + 7·71
T= Δ /2·49 + 7·97
ATLANTIS W
CARYN E
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
CARYN
ATLANTIS
DEPTH, fathoms
DISTANCE, km
OCEAN
(1·77)
3·49
5·45
DEPTH, km


PROFILE 44; 1955 CRUISE
TRAVEL TIME, sec
T= Δ /4·53 + 8·90
T= Δ /5·06 + 9·53
T= Δ /4·17 + 8·73
T= Δ /5·22 + 9·93
T= Δ /3·18 + 8·36
T= Δ /2·75 + 7·83
ATLANTIS E
CARYN W
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
CARYN
ATLANTIS
DEPTH, fathoms
DISTANCE, km
OCEAN
(1·70)
4·51
6·62
7·85
DEPTH, km

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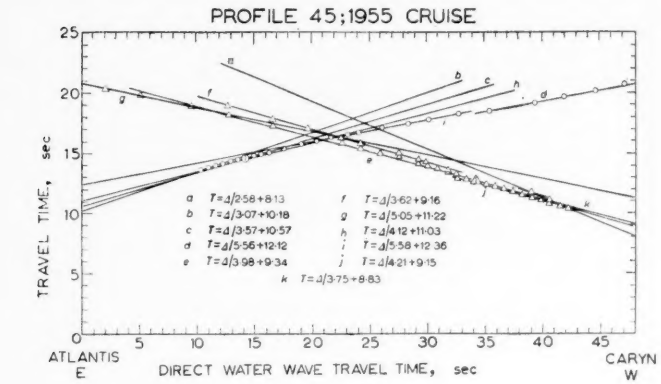
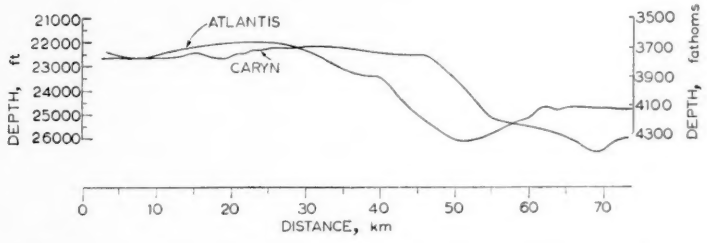
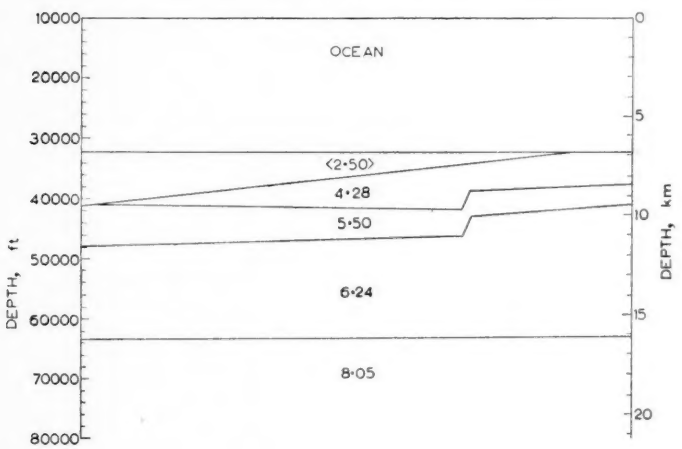

PROFILE 45;1955 CRUISE
TRAVEL TIME, sec
DIRECT WATER WAVE TRAVEL TIME, sec
ATLANTIS E
CARYN W
a T=Δ/2·58+8·13
b T=Δ/3·07+10·18
c T=Δ/3·57+10·57
d T=Δ/5·56+12·12
e T=Δ/3·98+9·34
f T=Δ/3·62+9·16
g T=Δ/5·05+11·22
h T=Δ/4·12+11·03
i T=Δ/5·58+12·36
j T=Δ/4·21+9·15
k T=Δ/3·75+8·83


ATLANTIS
CARYN
DEPTH, ft
DEPTH, fathoms
DISTANCE, km


OCEAN
<2·50>
4·28
5·50
6·24
8·05
DEPTH, ft
DEPTH, km

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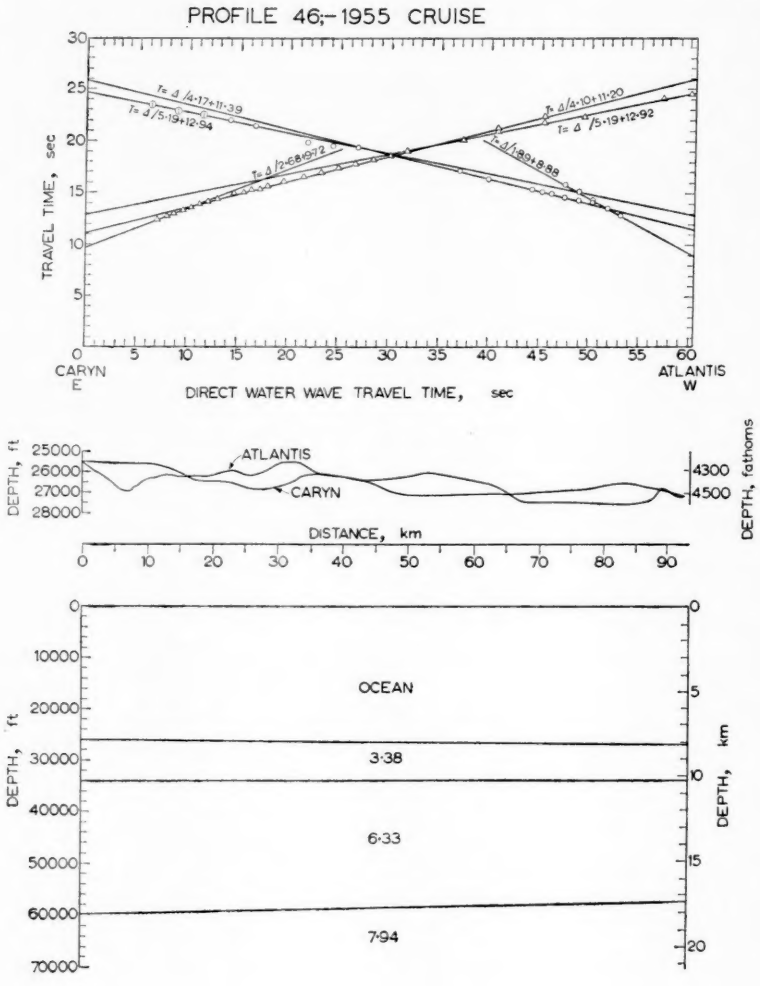
PROFILE 46;–1955 CRUISE
TRAVEL TIME, sec
T= Δ/4·17+11·39
T= Δ/5·19+12·94
T= Δ/2·68+9·72
T= Δ/4·10+11·20
T= Δ/5·19+12·92
T= Δ/1·90+8·88
CARYN
E
ATLANTIS
W
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
ATLANTIS
CARYN
DEPTH, fathoms
DISTANCE, km
DEPTH, ft
OCEAN
3·38
6·33
7·94
DEPTH, km

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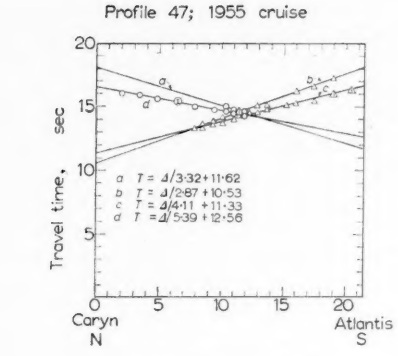
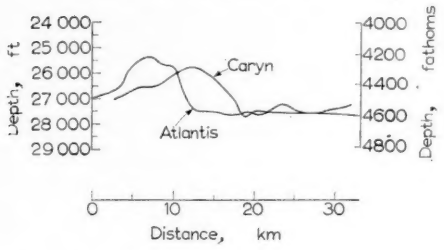
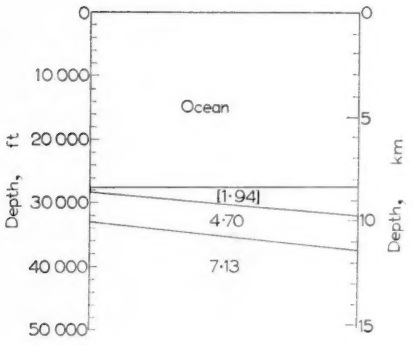

Profile 47; 1955 cruise
Travel time, sec
a T = Δ/3·32 + 11·62
b T = Δ/2·87 + 10·53
c T = Δ/4·11 + 11·33
d T = Δ/5·39 + 12·56
Caryn N
Atlantis S
Direct water wave travel time, sec


Depth, ft
Depth, fathoms
Caryn
Atlantis
Distance, km


Ocean
[1·94]
4·70
7·13
Depth, ft
Depth, km

deepest layer in *9* could be made to agree more closely with the 6·13 km/sec layer in *10* by assuming a steeper northward dip.

11, *12*. Topographic corrections were applied assuming a sloping base line from 1420 fathoms at the west end of *11* to 720 fathoms at the east end of *12*. These profiles were greatly complicated by a strong westerly drift which apparently offset the shooting tracks by 10–15 km. This undoubtably reduced the accuracy of the results appreciably, and the section shows, at best, only the general structural configuration.

13, *14*, 15. Topographic corrections were applied for sloping base lines which approximate the topography in profiles *13* and *14*. A level base line at a depth of 700 fathoms was assumed for profile *15*. The computations according to this assumption produced the section partially represented by the dashed lines. The re-adjustment of the interfaces (solid lines) show the actual structure. In these profiles some complications and uncertainties were introduced by a drift of approximately 7 km in the direction of the shot lines. This is clearly shown by the offset in the two fathograms.

16. Topographic corrections were applied for a level base line 18 fathoms deep. The two fathograms differ somewhat here because the *Bear*'s shooting run was approximately 1 km east of *Atlantis*. After topographic corrections were made there were still high points in the region of the topographic low in both sets of records. The structure shown in the section accounts for these points and is suggested by the observed topography. The section does not show the depression in the two upper layers.

17. The bottom topography is irregular along this profile but the refraction lines are well determined. The overlying materials with velocities 2·04, 3·85, and 5·48 km/sec are thick under this profile. The crustal arrival is well defined by a first arrival refraction line on one-half of the profile. It appears as a masked refraction line on the other half.

18. The bottom topography is irregular along this profile. The crustal refraction line is again masked. As on profiles *6* and *17* it has been included in the calculations. The other refraction lines are well determined.

19. Topographic corrections were applied for a level base line 30 fathoms deep. These corrections removed the effects of the depression near the *Atlantis* receiving position, indicating that approximately the same relief is present in the deeper interfaces.

20. The crustal refraction is masked but has been included in the calculations. The mantle refraction line is defined, but its velocity is not well determined.

21. Topographic corrections were applied for a base line which slopes from 670 fathoms in the north to 1060 fathoms in the south. The topography, assumed to be approximately duplicated in the deeper interfaces, is not shown in the section.

22, *23*. Require no comment.

24. Topographic corrections were applied for a sloping base line from 1820 fathoms at the east end to 2340 fathoms at the west. A westerly drift caused the deviation in the two echo sounder records. The second, third and fourth layers were not detected in the *Atlantis* records but were assumed to be masked. The fourth layer (4·95 km/sec) was almost masked at the east end; but there is additional evidence for its presence since a similar velocity was measured at profiles 9, 10, 30, 31, *22* and *23*.

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25. The base line for topographic corrections for this profile slopes from a depth of 2700 fathoms at the east end to 2780 fathoms at the west. The determination of three high-velocity layers here may be questionable. A reasonably good fit of the data may be achieved with two lines representing velocities of about 6·4 and 7·8 km/sec. However, the three-layer interpretation which is shown gives a slightly better fit and is in better agreement with the other data in the area.

26. Topographic corrections were applied for a level base line at 2720 fathoms. The three high-velocity layers were well determined here by both compressional and transformed shear waves. The *Atlantis* records in particular contain an unusually strong set of shear wave arrivals. These are shown in Fig. 8, which is a tracing of one low frequency trace from each record, spaced according to shot distance. The shear wave arrivals are labelled G_s.

27. Topographic corrections were made for an assumed level base line at 2450 fathoms depth. The three high-velocity lines are reasonably well determined, but it is possible that a somewhat different interpretation might be made. There is little doubt that the 6·5 km/sec velocity is correct, and it also seems certain that the highest velocity is near 7·9 km/sec; but it is difficult to determine positively whether there is a separate intermediate layer or a gradual change between the 6·5 and 7·9 km/sec layers.

28. Requires no comment.

29. There is considerable change in topography along this profile, but the lines were well determined. The mantle was not detected.

30. Requires no comment.

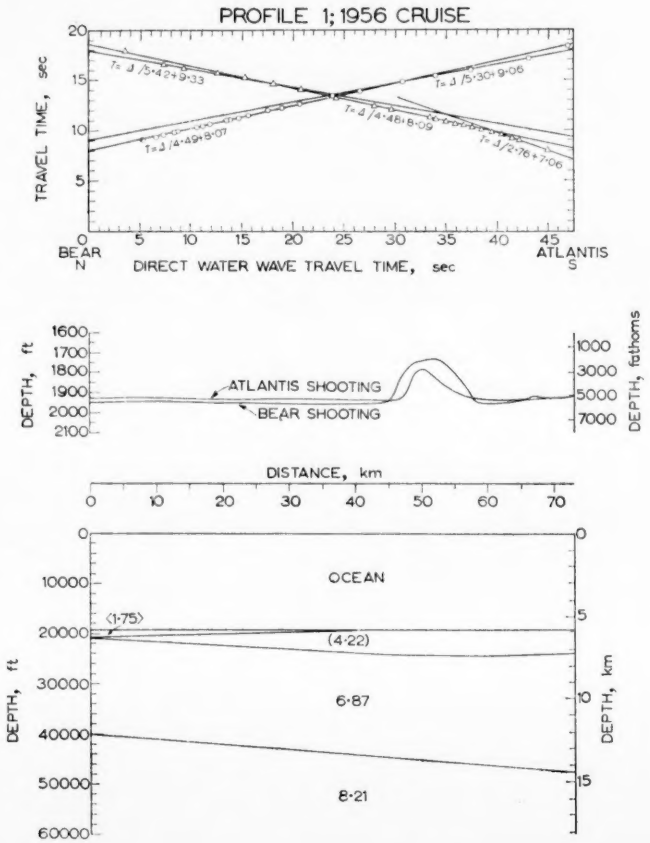
STRUCTURE CROSS-SECTIONS

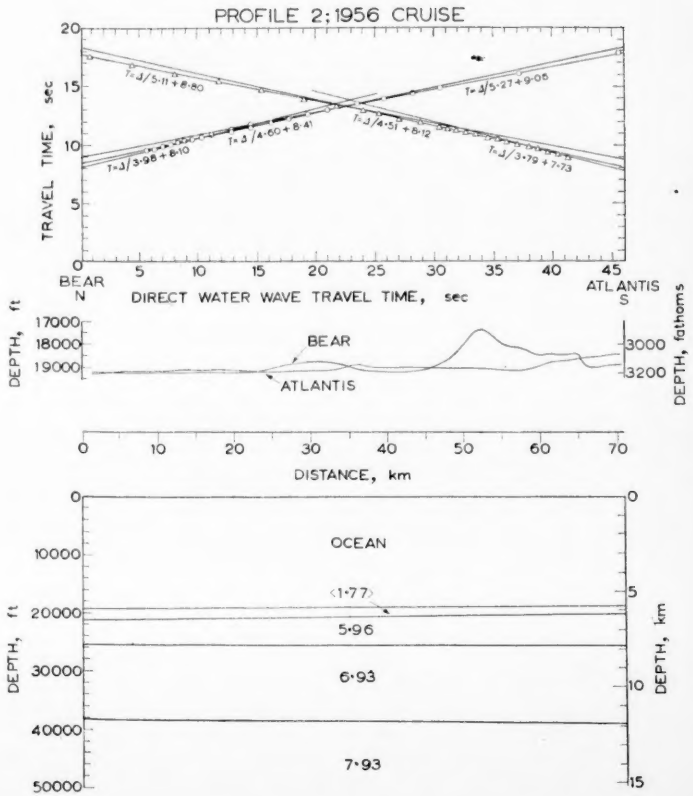
The geophysical results have been summarized in a number of structure cross-sections. Their locations are shown in Fig. 2. We consider these cross-sections a convenient pictorial manner in which to present the results. Most of the features on them are quite clear and need little or no comment. Some of the more striking results are mentioned and discussed below.

Section 1

Section 1, shown in Fig. 14, begins near the middle of the Venezuelan basin and crosses the northern end of the Aves swell, the inner volcanic arc of the Lesser Antilles near Nevis, the outer arc between Antigua and Barbuda, the south-eastern end of the Puerto Rico trench, and ends about 140 miles north-east of Barbuda. The section is about 500 miles long and includes the data from sixteen profiles. With a few exceptions the measured velocities can be separated into general groups represented by the five layers in the cross-section.

The entire crustal section was measured at profiles *26* and *27* in the Venezuelan basin and at profiles *4*, *5*, *6*, and *17* in the Atlantic basin outside the island arc. At the other profiles the mantle was not reached, although most of them measured the section down to the high velocity crustal layer. The velocities found for this layer vary between 6·0 and 7·6 km/sec, with most of the variability coming in the Caribbean and island arc profiles. In general, in the interpretation of the travel time data for the Venezuelan basin profiles, the best fit is achieved with two lines representing the crustal material: one for a velocity


PROFILE 1; 1956 CRUISE
TRAVEL TIME, sec
T= Δ /5·42+9·33
T= Δ /5·30+9·06
T= Δ /4·49+8·07
T= Δ /4·48+8·09
T= Δ /2·76+7·06
BEAR N
ATLANTIS S
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
DEPTH, fathoms
ATLANTIS SHOOTING
BEAR SHOOTING
DISTANCE, km
OCEAN
⟨1·75⟩
(4·22)
6·87
8·21
DEPTH, km


PROFILE 2; 1956 CRUISE
TRAVEL TIME, sec
T= Δ/5·11+8·80
T= Δ/5·27+9·05
T= Δ/4·60+8·41
T= Δ/4·51+8·12
T= Δ/3·98+8·10
T= Δ/3·79+7·73
BEAR N
ATLANTIS S
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
DEPTH, fathoms
BEAR
ATLANTIS
DISTANCE, km
OCEAN
⟨1·77⟩
5·96
6·93
7·93
DEPTH, km

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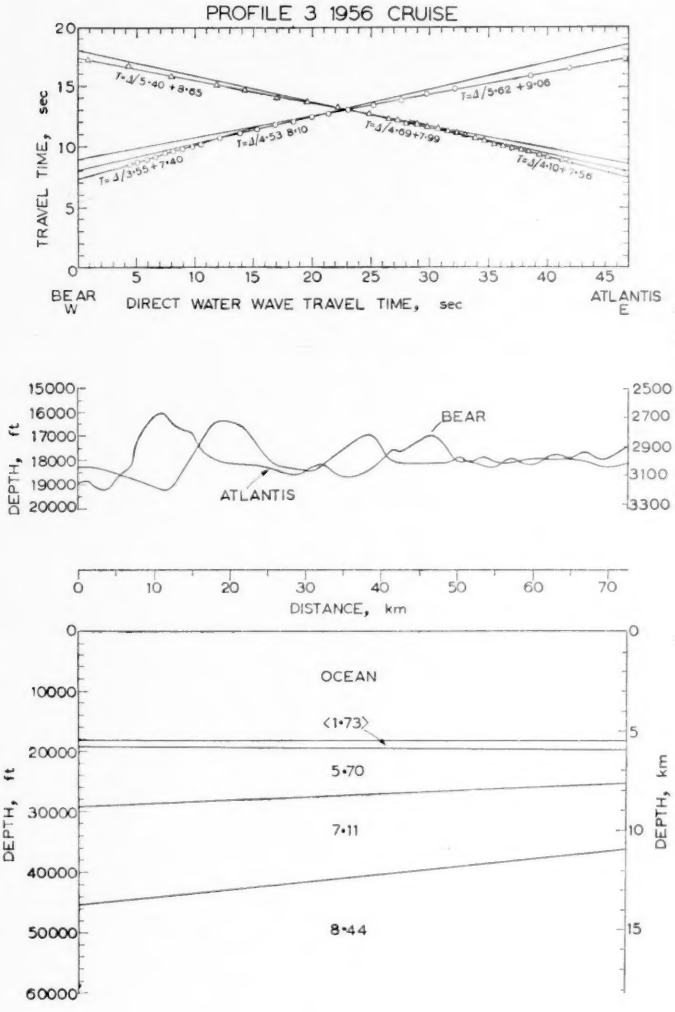
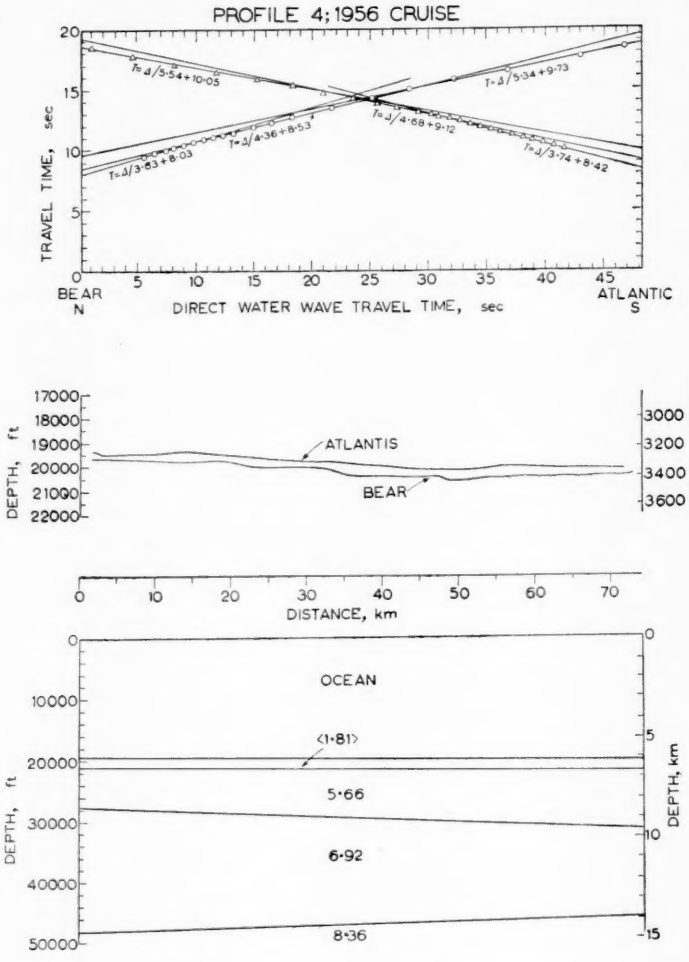

PROFILE 3 1956 CRUISE
TRAVEL TIME, sec
T=Δ/5·40 +8·65
T=Δ/5·62 +9·06
T=Δ/4·53 8·10
T=Δ/4·09+7·99
T=Δ/3·55+7·40
T=Δ/4·10+ 7·56
BEAR W
DIRECT WATER WAVE TRAVEL TIME, sec
ATLANTIS E
DEPTH, ft
BEAR
ATLANTIS
DEPTH, fathoms
DISTANCE, km
OCEAN
<1·73>
5·70
7·11
8·44
DEPTH, ft
DEPTH, km


PROFILE 4; 1956 CRUISE
TRAVEL TIME, sec
DIRECT WATER WAVE TRAVEL TIME, sec
BEAR N
ATLANTIC S
T=Δ/5·54+10·05
T=Δ/5·34+9·73
T=Δ/4·36+8·53
T=Δ/4·68+9·12
T=Δ/3·83+8·03
T=Δ/3·74+8·42
DEPTH, ft
DEPTH, fathoms
ATLANTIS
BEAR
DISTANCE, km
DEPTH, km
OCEAN
<1·81>
5·66
6·92
8·36

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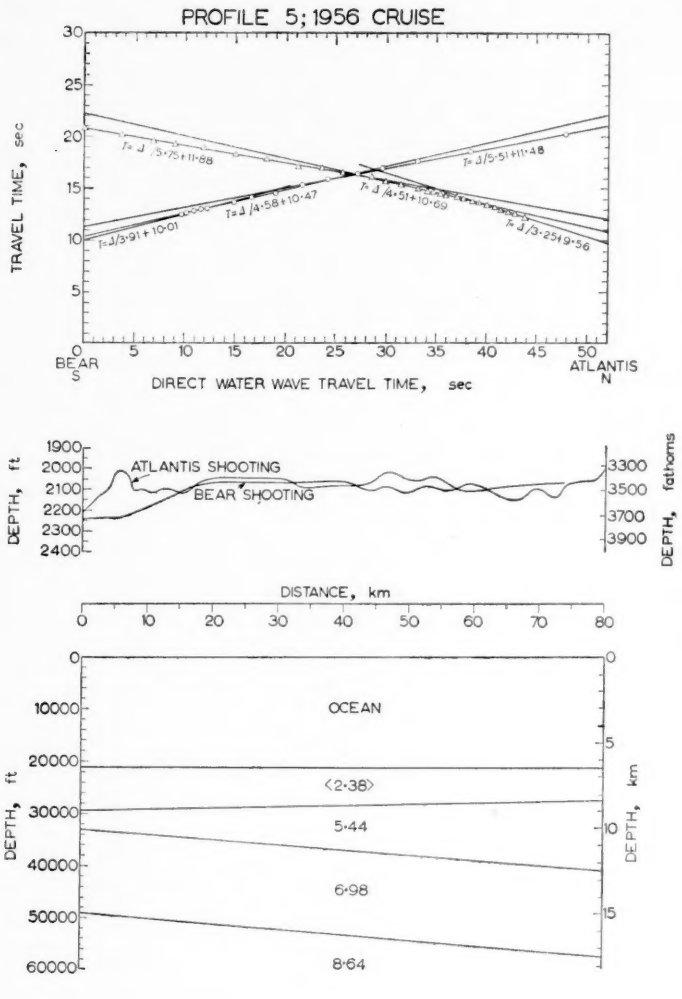
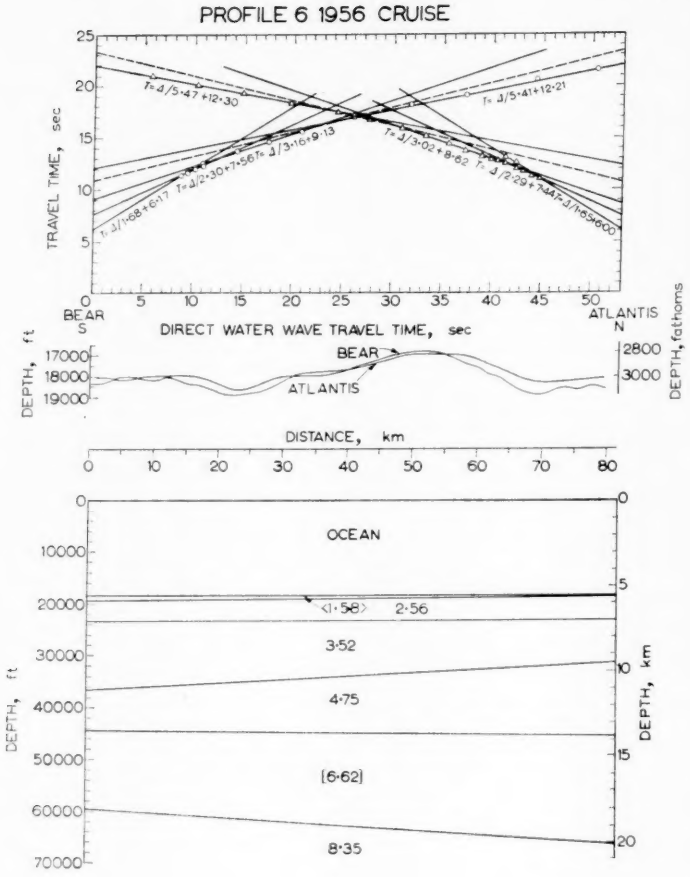

PROFILE 5; 1956 CRUISE
TRAVEL TIME, sec
T= Δ /5·75+11·88
T= Δ/5·51+11·48
T= Δ /4·58+10·47
T= Δ /4·51+10·69
T=Δ/3·91+10·01
T= Δ/3·2519·56
BEAR S
ATLANTIS N
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
ATLANTIS SHOOTING
BEAR SHOOTING
DEPTH, fathoms
DISTANCE, km
OCEAN
<2·38>
5·44
6·98
8·64
DEPTH, ft
DEPTH, km


PROFILE 6 1956 CRUISE
TRAVEL TIME, sec
T= Δ/5·47 +12·30
T= Δ/5·41+12·21
T= Δ/3·16+9·13
T= Δ/3·02+8·62
T= Δ/2·30+7·56
T= Δ/1·68+6·17
T= Δ/2·29+7·44
T= Δ/1·65+6·00
BEAR S
ATLANTIS N
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
DEPTH, fathoms
BEAR
ATLANTIS
DISTANCE, km
OCEAN
<1·58>
2·56
3·52
4·75
[6·62]
8·35
DEPTH, km

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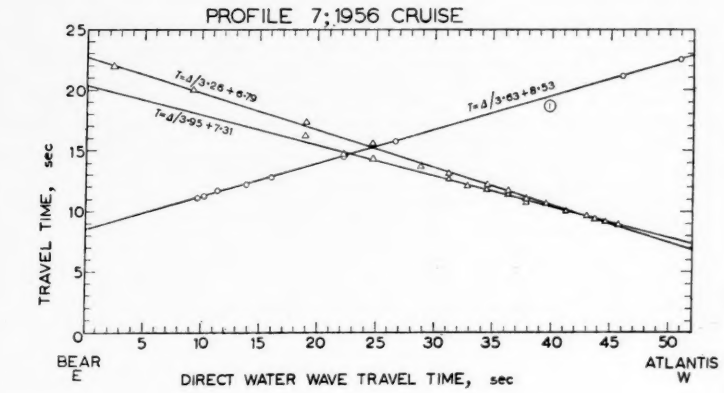
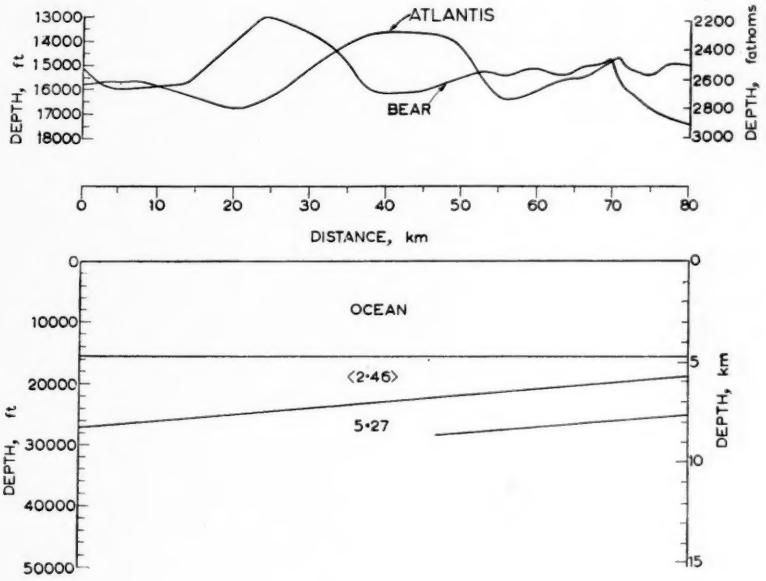
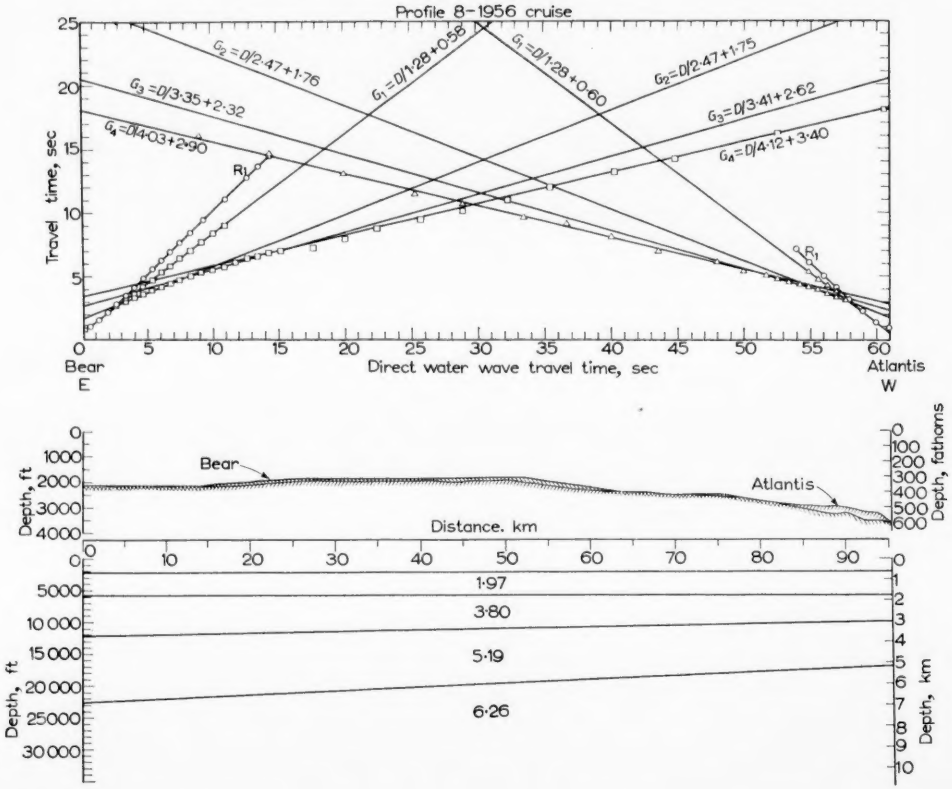

PROFILE 7; 1956 CRUISE
TRAVEL TIME, sec
T=Δ/3·26+6·79
T=Δ/3·95+7·31
T=Δ/3·63+8·53
BEAR E
ATLANTIS W
DIRECT WATER WAVE TRAVEL TIME, sec


ATLANTIS
BEAR
DEPTH, ft
DEPTH, fathoms
DISTANCE, km
OCEAN
⟨2·46⟩
5·27
DEPTH, ft
DEPTH, km


Profile 8–1956 cruise
$G_2 = D/2{\cdot}47 + 1{\cdot}76$
$G_1 = D/1{\cdot}28 + 0{\cdot}58$
$G_1 = D/1{\cdot}28 + 0{\cdot}60$
$G_2 = D/2{\cdot}47 + 1{\cdot}75$
$G_3 = D/3{\cdot}35 + 2{\cdot}32$
$G_3 = D/3{\cdot}41 + 2{\cdot}62$
$G_4 = D/4{\cdot}03 + 2{\cdot}90$
$G_4 = D/4{\cdot}12 + 3{\cdot}40$
R_1
R_1
Travel time, sec
Direct water wave travel time, sec
Bear
E
Atlantis
W
Bear
Atlantis
Depth, ft
Depth, fathoms
Distance. km
1·97
3·80
5·19
6·26
Depth, ft
Depth, km

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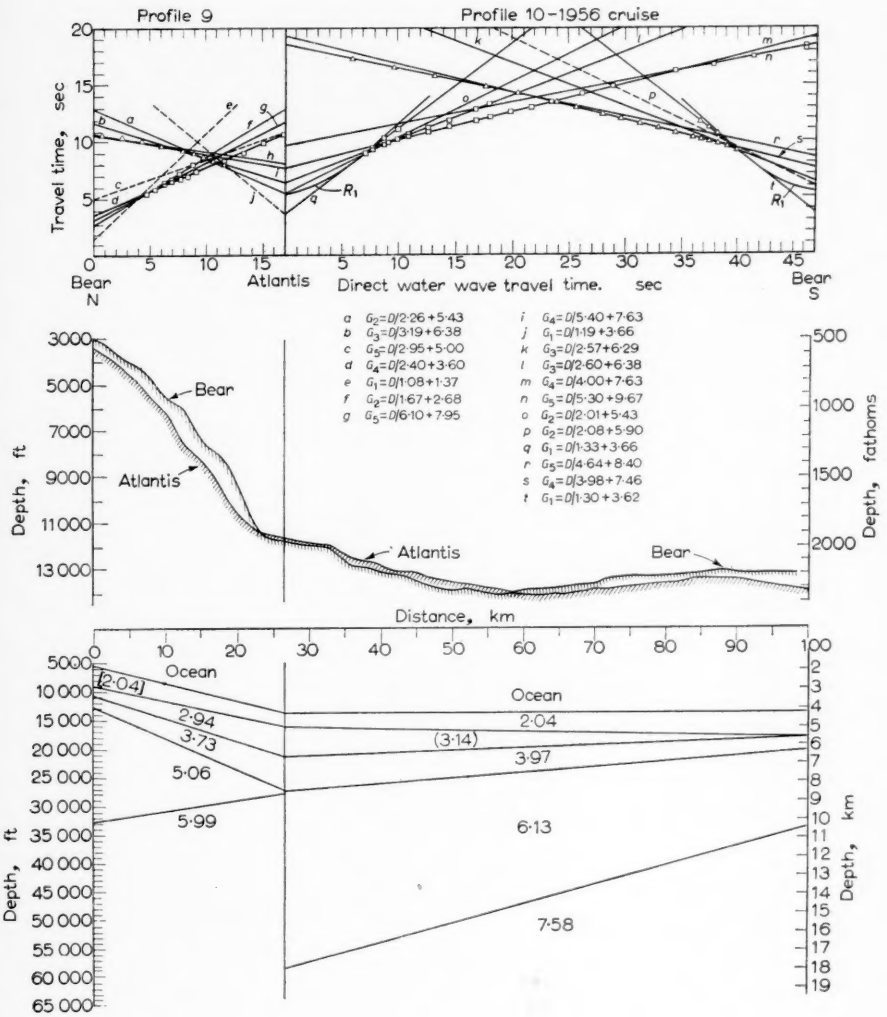
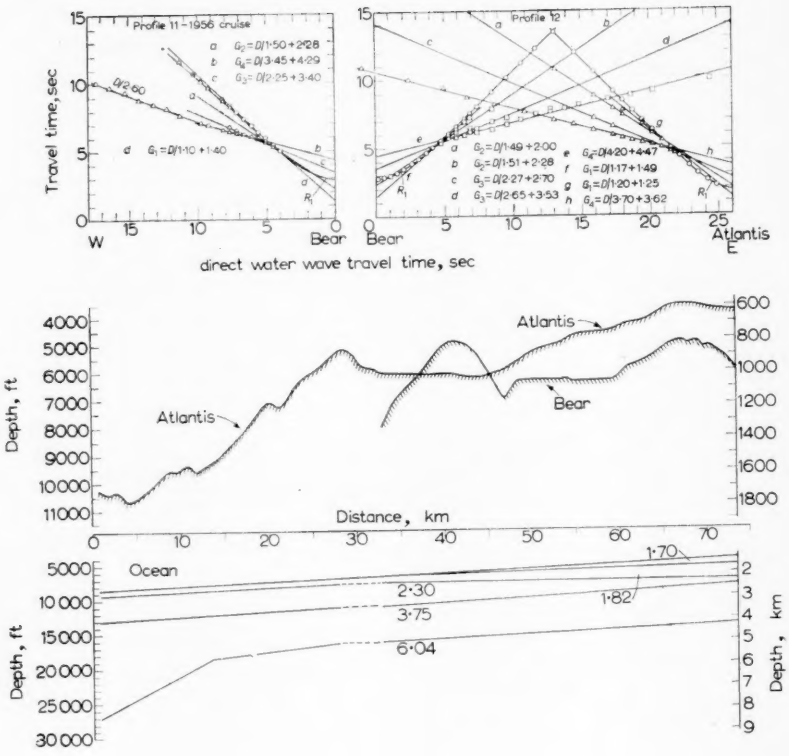
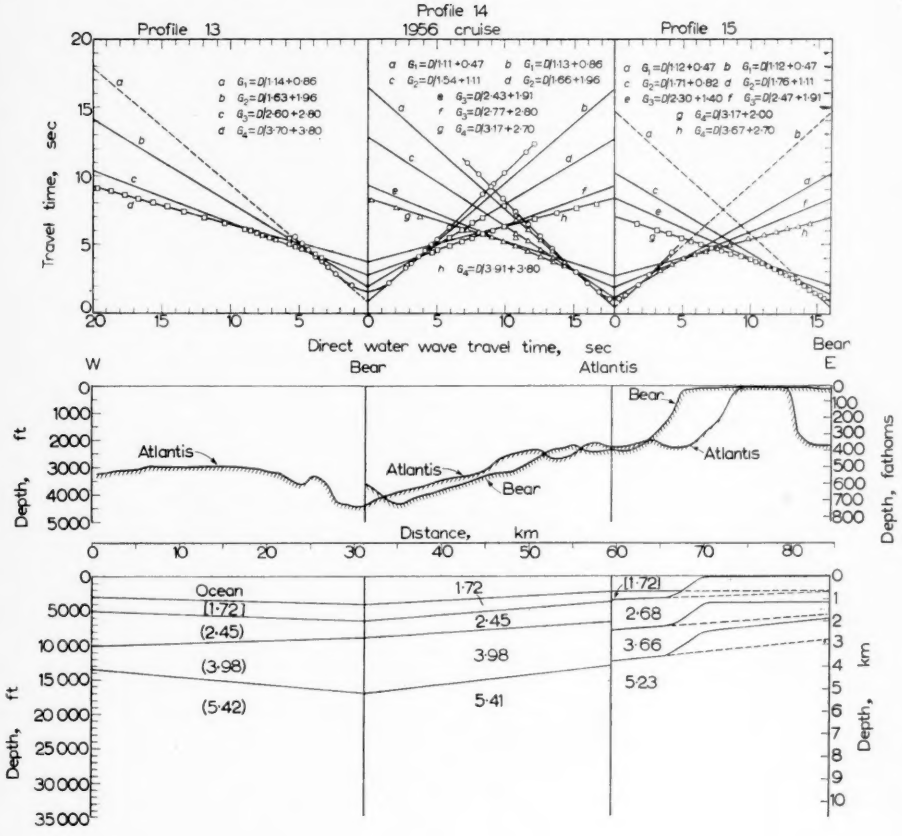

Profile 9
Profile 10–1956 cruise
Travel time, sec
Bear N
Atlantis
Direct water wave travel time. sec
Bear S
a G2=D/2·26+5·43
b G3=D/3·19+6·38
c G5=D/2·95+5·00
d G4=D/2·40+3·60
e G1=D/1·08+1·37
f G2=D/1·67+2·68
g G5=D/6·10+7·95
i G4=D/5·40+7·63
j G1=D/1·19+3·66
k G3=D/2·57+6·29
l G3=D/2·60+6·38
m G4=D/4·00+7·63
n G5=D/5·30+9·67
o G2=D/2·01+5·43
p G2=D/2·08+5·90
q G1=D/1·33+3·66
r G5=D/4·64+8·40
s G4=D/3·98+7·46
t G1=D/1·30+3·62
Depth, ft
Depth, fathoms
Bear
Atlantis
Distance, km
Ocean
2·04
2·94
3·73
5·06
5·99
(3·14)
3·97
6·13
7·58
Depth, km


Profile 11 – 1956 cruise
Profile 12
Travel time, sec
direct water wave travel time, sec
W
Bear
Bear
Atlantis
E
Depth, ft
Depth, fathoms
Atlantis
Bear
Distance, km
Ocean
1·70
2·30
1·82
3·75
6·04
Depth, km


Profile 13
Profile 14
1956 cruise
Profile 15
Travel time, sec
Direct water wave travel time, sec
W
Bear
Atlantis
Bear
E
Depth, ft
Depth, fathoms
Atlantis
Atlantis
Bear
Bear
Atlantis
Distance, km
Ocean
[1·72]
(2·45)
(3·98)
(5·42)
1·72
2·45
3·98
5·41
[1·72]
2·68
3·66
5·23
Depth, ft
Depth, km

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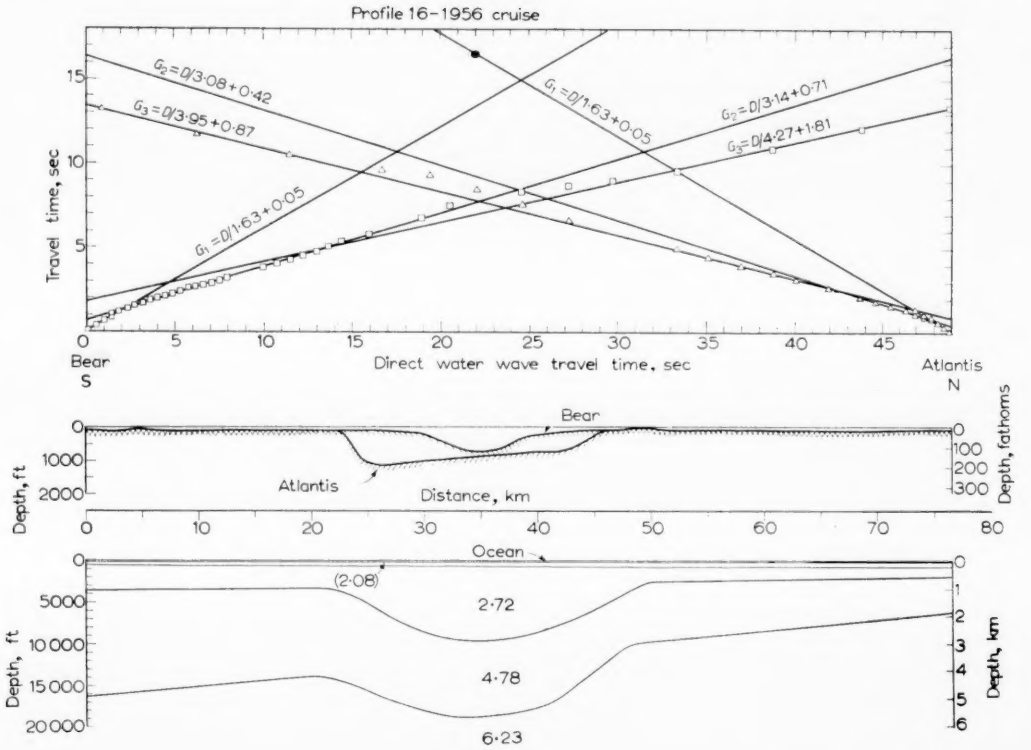
Profile 16–1956 cruise
$G_2 = D/3{\cdot}08 + 0{\cdot}42$
$G_3 = D/3{\cdot}95 + 0{\cdot}87$
$G_1 = D/1{\cdot}63 + 0{\cdot}05$
$G_1 = D/1{\cdot}63 + 0{\cdot}05$
$G_2 = D/3{\cdot}14 + 0{\cdot}71$
$G_3 = D/4{\cdot}27 + 1{\cdot}81$
Travel time, sec
Direct water wave travel time, sec
Bear
S
Atlantis
N
Bear
Atlantis
Distance, km
Depth, ft
Depth, fathoms
Ocean
(2·08)
2·72
4·78
6·23
Depth, km

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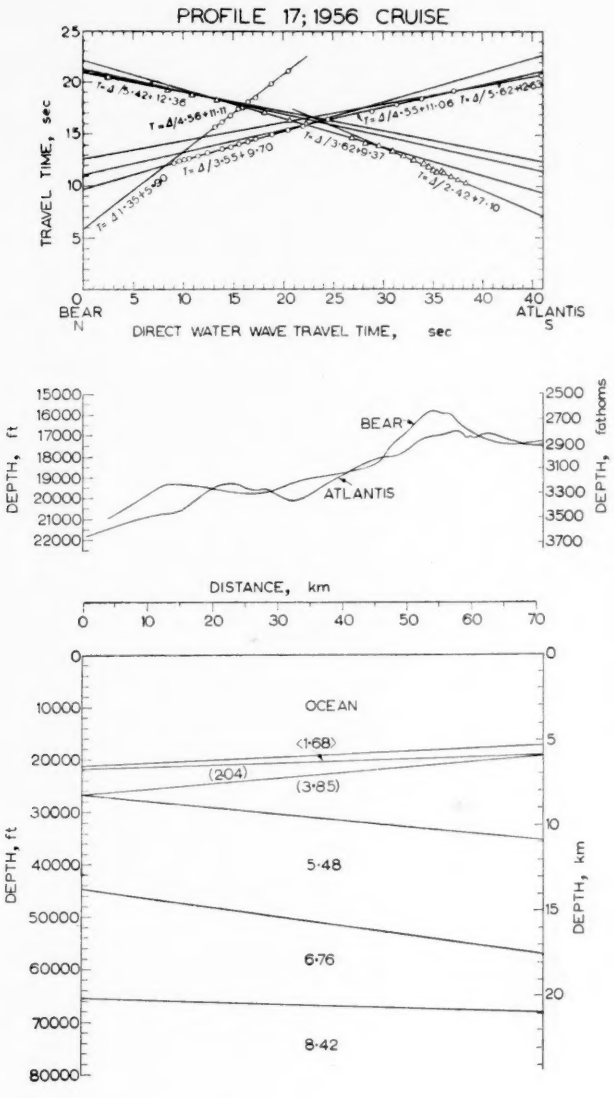
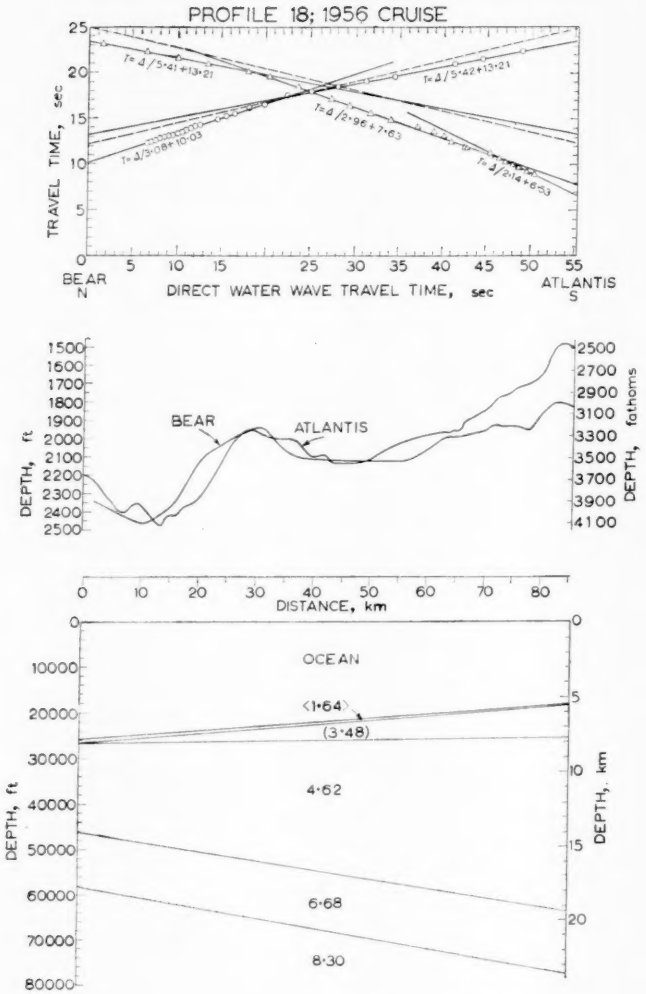
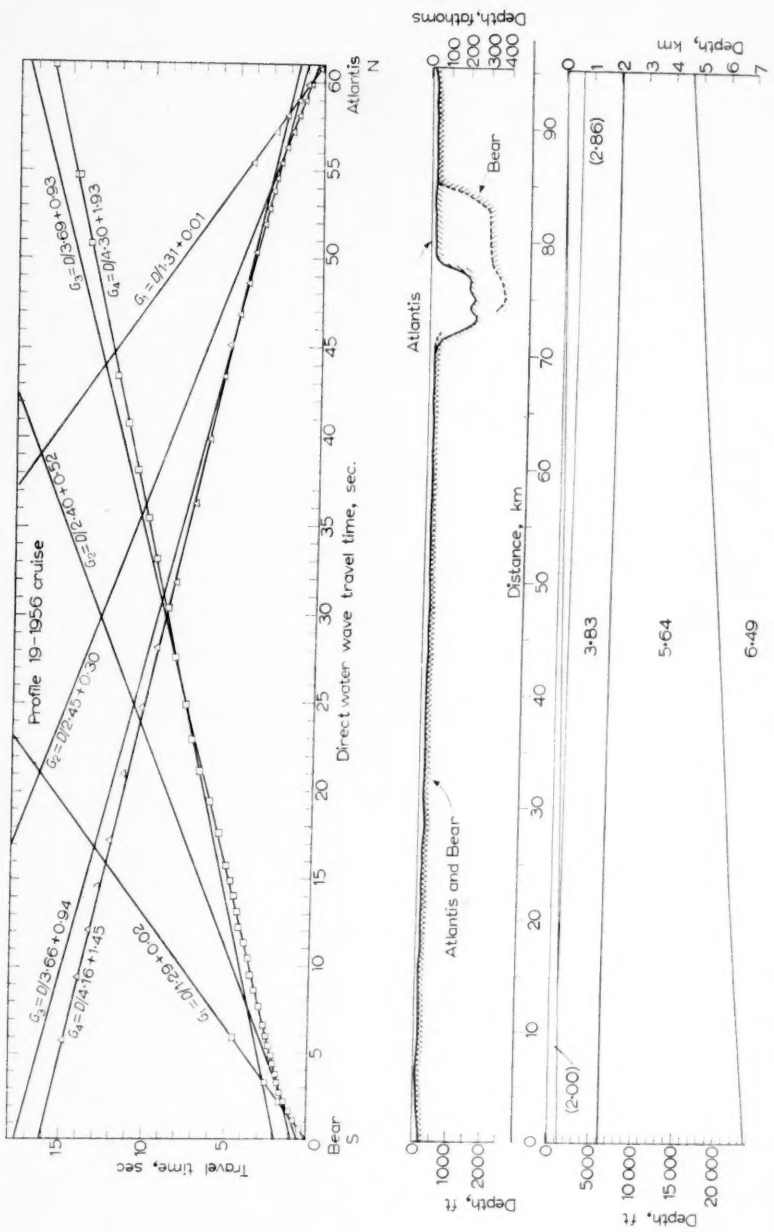
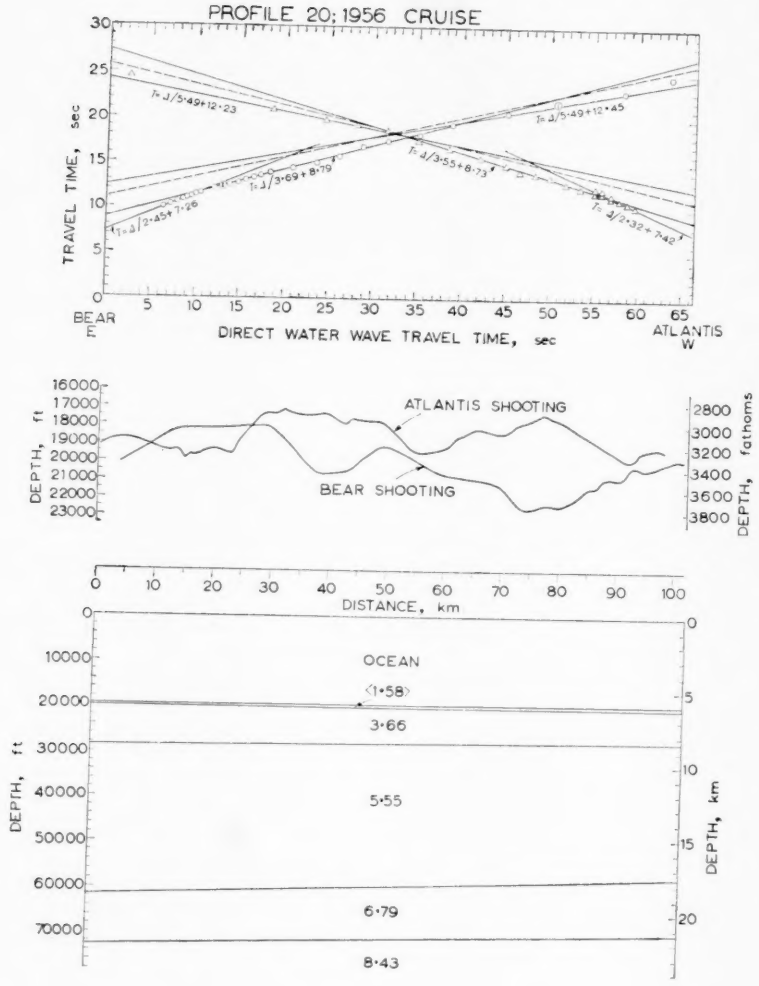
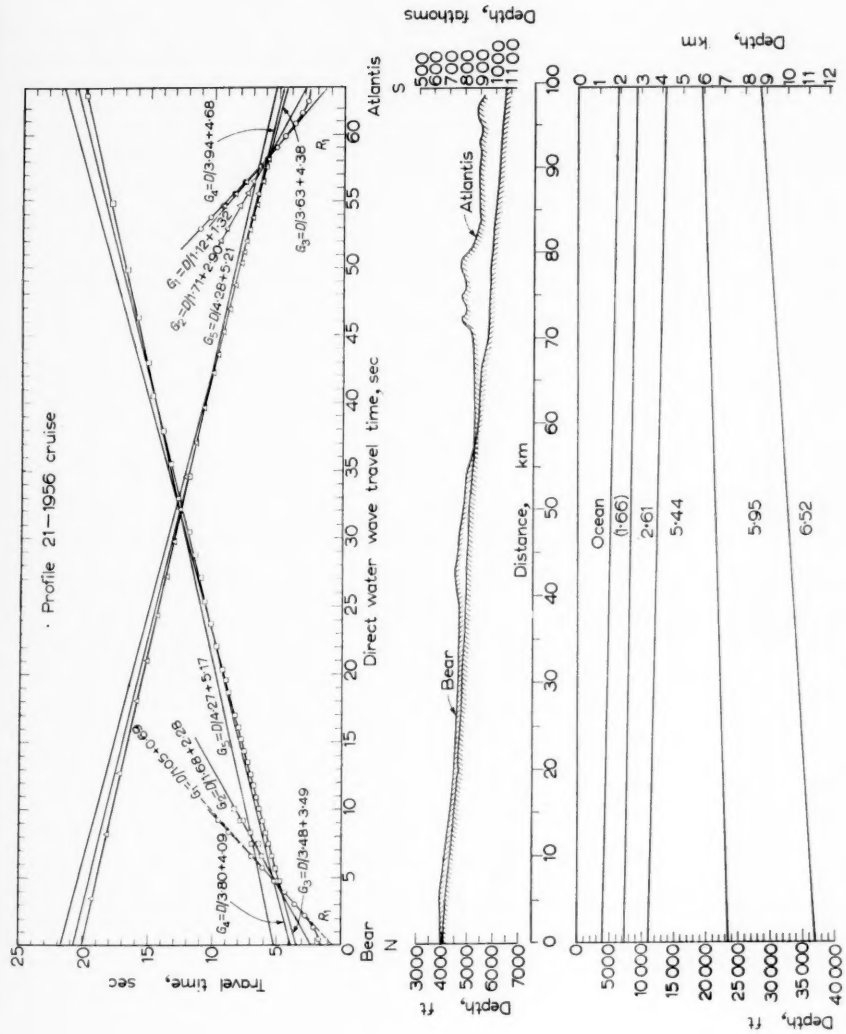
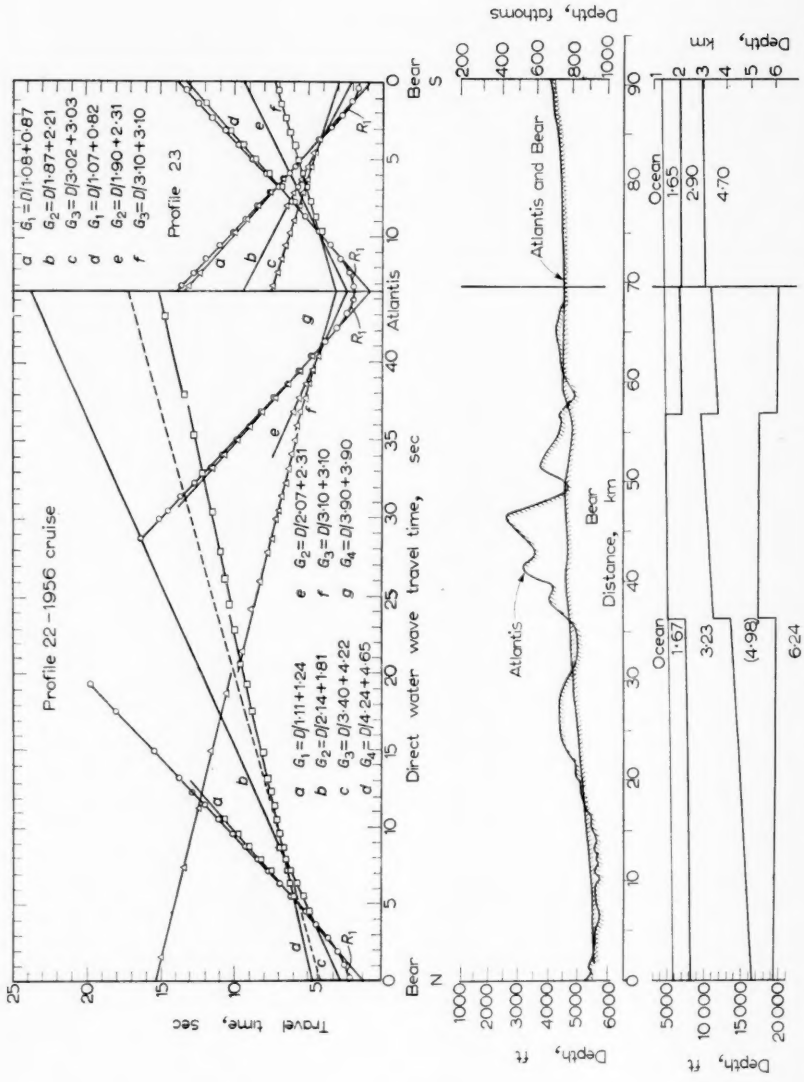

PROFILE 17; 1956 CRUISE
TRAVEL TIME, sec
T=Δ/5·42+12·38
T=Δ/4·56+11·11
T=Δ/4·55+11·06
T=Δ/5·62+12·63
T=Δ/3·62+9·37
T=Δ/3·55+9·70
T=Δ/2·42+7·10
T=Δ/1·35+5·00
BEAR
N
ATLANTIS
S
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
DEPTH, fathoms
BEAR
ATLANTIS
DISTANCE, km
OCEAN
⟨1·68⟩
(2·04)
(3·85)
5·48
6·76
8·42
DEPTH, km

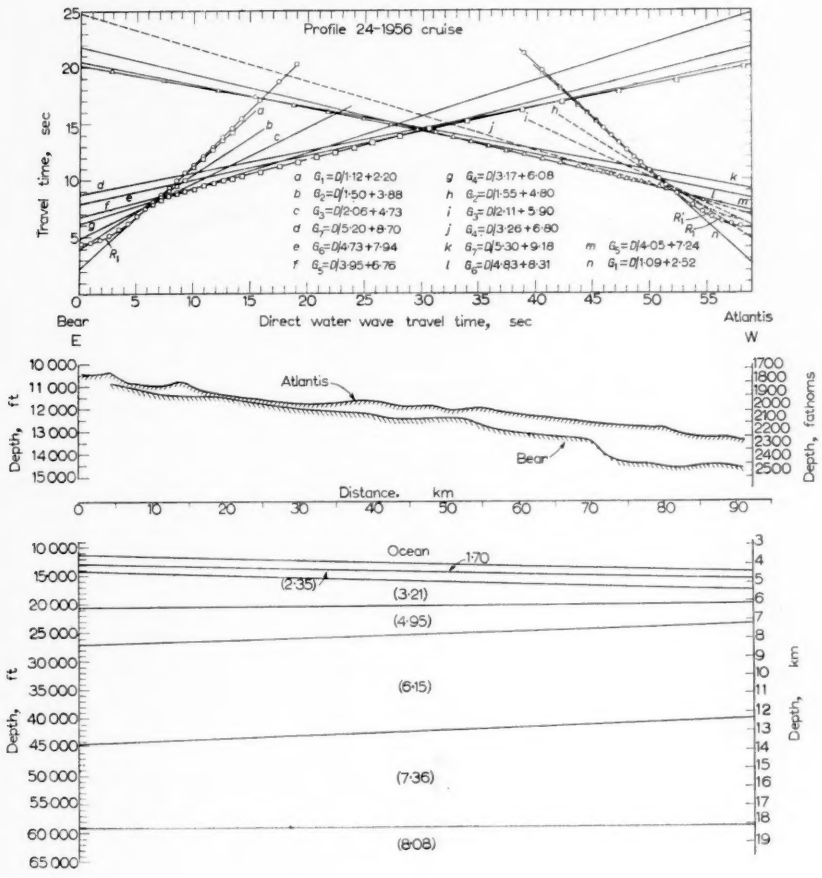

PROFILE 18; 1956 CRUISE
TRAVEL TIME, sec
T=Δ/5·41+13·21
T=Δ/5·42+13·21
T=Δ/2·96+7·63
T=Δ/3·08+10·03
T=Δ/2·14+6·53
BEAR N
ATLANTIS S
DIRECT WATER WAVE TRAVEL TIME, sec
DEPTH, ft
DEPTH, fathoms
BEAR
ATLANTIS
DISTANCE, km
OCEAN
<1·64>
(3·48)
4·62
6·68
8·30
DEPTH, ft
DEPTH, km

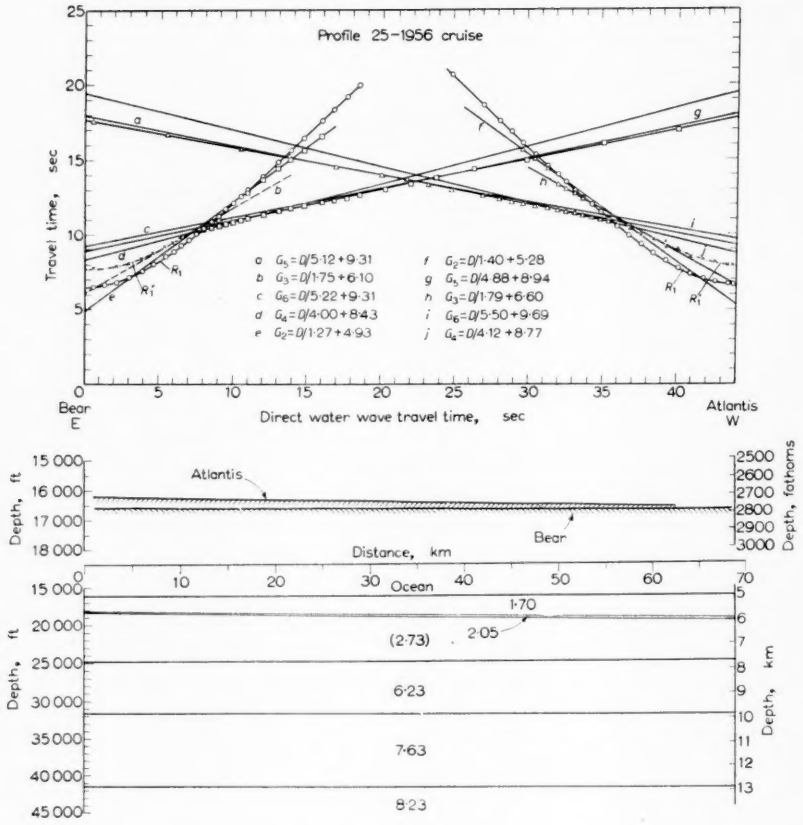

Profile 19-1956 cruise
Direct water wave travel time, sec.
Travel time, sec
Bear
Atlantis
N
S
$G_3=0/3{\cdot}66+0{\cdot}94$
$G_4=0/4{\cdot}16+1{\cdot}45$
$G_5=0/4{\cdot}29+2{\cdot}00$
$G_2=0/2{\cdot}45+0{\cdot}30$
$G_2=0/2{\cdot}40+0{\cdot}52$
$G_3=0/3{\cdot}69+0{\cdot}93$
$G_4=0/4{\cdot}30+1{\cdot}93$
$G_1=0/1{\cdot}31+0{\cdot}01$
Depth, fathoms
Atlantis
Bear
Atlantis and Bear
Distance, km
Depth, ft
Depth, km
(2·00)
(2·86)
3·83
5·64
6·49


PROFILE 20; 1956 CRUISE
TRAVEL TIME, sec
DIRECT WATER WAVE TRAVEL TIME, sec
BEAR E
ATLANTIS W
T= Δ/5·49+12·23
T= Δ/5·49+12·45
T= Δ/3·69+8·19
T= Δ/3·55+8·73
T= Δ/2·45+7·26
T= Δ/2·32+7·42
DEPTH, ft
DEPTH, fathoms
ATLANTIS SHOOTING
BEAR SHOOTING
DISTANCE, km
DEPTH, km
OCEAN
⟨1·58⟩
3·66
5·55
6·79
8·43


Profile 21—1956 cruise
Travel time, sec
Direct water wave travel time, sec
Bear
N
Atlantis
S
$G_1=0/1\cdot12+1\cdot38$
$G_2=0/1\cdot71+2\cdot90$
$G_3=0/3\cdot63+4\cdot38$
$G_4=0/3\cdot94+4\cdot68$
$G_5=0/4\cdot26+5\cdot21$
$G_1=0/3\cdot80+4\cdot09$
$G_2=0/1\cdot68+2\cdot28$
$G_3=0/3\cdot48+3\cdot49$
$G_4=0/1\cdot27+5\cdot17$
$G_5=0/0\cdot05+0\cdot68$
Depth, fathoms
Depth, ft
Distance, km
Depth, km
Depth, ft
Ocean
(1·66)
2·61
5·44
5·95
6·52


Profile 22–1956 cruise
Profile 23
Travel time, sec
Direct water wave travel time, sec
Bear N
Bear S
Atlantis
a G1=D/1·11+1·24
b G2=D/2·14+1·81
c G3=D/3·40+4·22
d G4=D/4·24+4·65
e G2=D/2·07+2·31
f G3=D/3·10+3·10
g G4=D/3·90+3·90
a G1=D/1·08+0·87
b G2=D/1·87+2·21
c G3=D/3·02+3·03
d G1=D/1·07+0·82
e G2=D/1·90+2·31
f G3=D/3·10+3·10
Depth, ft
Depth, fathoms
Atlantis and Bear
Distance, km
Ocean
1·67
3·23
(4·98)
6·24
1·65
2·90
4·70
Depth, km


Profile 24-1956 cruise
Travel time, sec
Direct water wave travel time, sec
Bear
E
Atlantis
W
a G1=0/1·12+2·20
b G2=0/1·50+3·88
c G3=0/2·06+4·73
d G7=0/5·20+8·70
e G6=0/4·73+7·94
f G5=0/3·95+6·76
g G4=0/3·17+6·08
h G2=0/1·55+4·80
i G3=0/2·11+5·90
j G4=0/3·26+6·80
k G7=0/5·30+9·18
l G6=0/4·83+8·31
m G5=0/4·05+7·24
n G1=0/1·09+2·52
Atlantis
Bear
Depth, ft
Depth, fathoms
Distance, km
Ocean
1·70
(2·35)
(3·21)
(4·95)
(6·15)
(7·36)
(8·08)
Depth, km


Profile 25–1956 cruise
Travel time, sec
Direct water wave travel time, sec
Bear E
Atlantis W
a $G_5=D/5{\cdot}12+9{\cdot}31$
b $G_3=D/1{\cdot}75+6{\cdot}10$
c $G_6=D/5{\cdot}22+9{\cdot}31$
d $G_4=D/4{\cdot}00+8{\cdot}43$
e $G_2=D/1{\cdot}27+4{\cdot}93$
f $G_2=D/1{\cdot}40+5{\cdot}28$
g $G_5=D/4{\cdot}88+8{\cdot}94$
h $G_3=D/1{\cdot}79+6{\cdot}60$
i $G_6=D/5{\cdot}50+9{\cdot}69$
j $G_4=D/4{\cdot}12+8{\cdot}77$
Depth, ft
Depth, fathoms
Atlantis
Bear
Distance, km
Ocean
1·70
2·05
(2·73)
6·23
7·63
8·23
Depth, km

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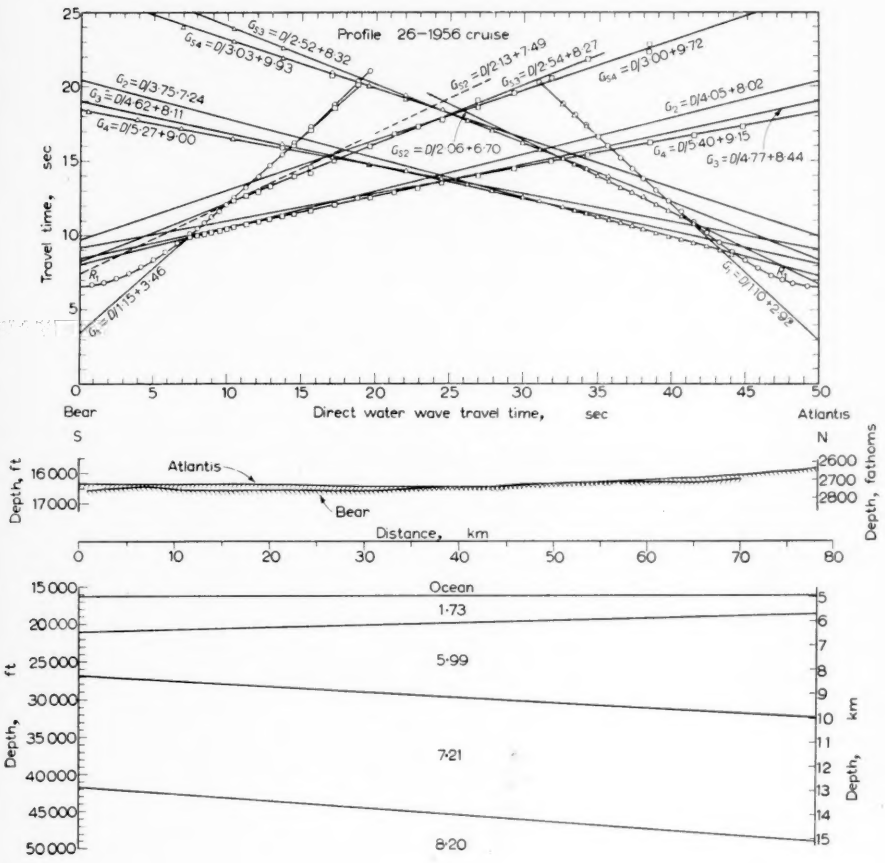
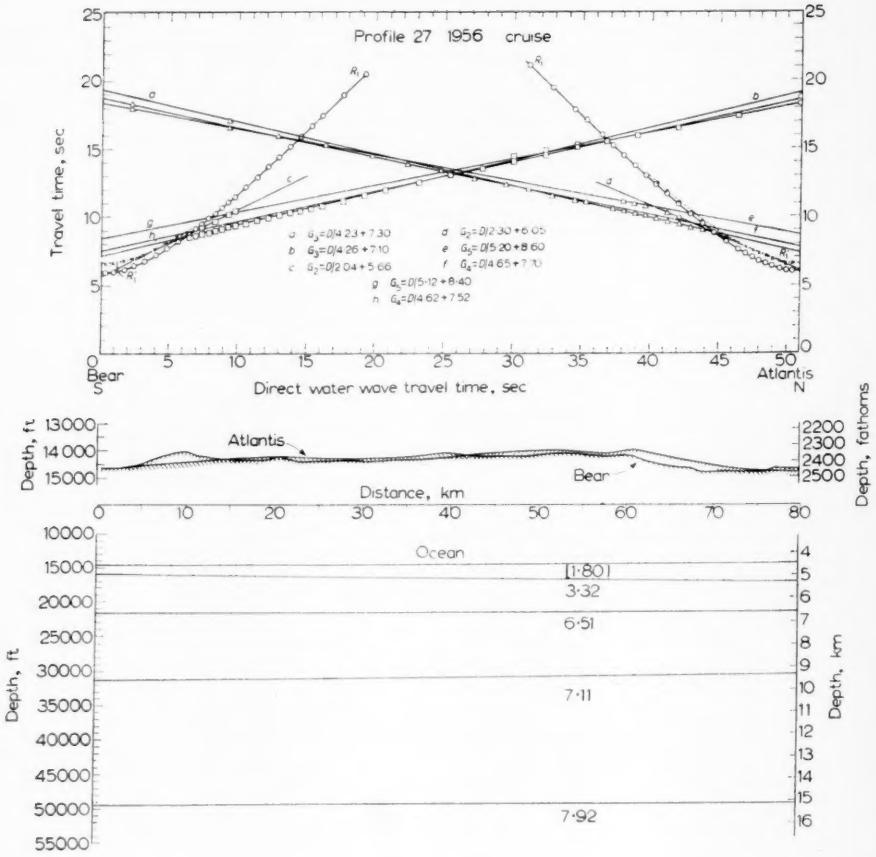

Profile 26–1956 cruise
$G_{S4}=0/3{\cdot}03+9{\cdot}93$
$G_{S3}=0/2{\cdot}52+8{\cdot}32$
$G_{S3}=0/2{\cdot}13+7{\cdot}49$
$G_{S3}=0/2{\cdot}54+8{\cdot}27$
$G_{S4}=0/3{\cdot}00+9{\cdot}72$
$G_2=0/3{\cdot}75+7{\cdot}24$
$G_3=0/4{\cdot}62+8{\cdot}11$
$G_4=0/5{\cdot}27+9{\cdot}00$
$G_{S2}=0/2{\cdot}06+6{\cdot}70$
$G_2=0/4{\cdot}05+8{\cdot}02$
$G_4=0/5{\cdot}40+9{\cdot}15$
$G_3=0/4{\cdot}77+8{\cdot}44$
$G_1=0/1{\cdot}15+3{\cdot}46$
$G_1=0/1{\cdot}10+2{\cdot}93$
Travel time, sec
Direct water wave travel time, sec
Bear
Atlantis
S
N
Depth, ft
Depth, fathoms
Distance, km
Ocean
1·73
5·99
7·21
8·20
Depth, km


Profile 27 1956 cruise
Travel time, sec
Direct water wave travel time, sec
Bear
Atlantis
S
N
a G3=0/4 23 + 7 30
b G3=0/4 26 + 7 10
c G2=0/2 04 + 5 66
d G2=0/2 30 + 6 05
e G3=0/5 20 + 8 60
f G4=0/4 65 + 7 70
g G5=0/5·12 + 8·40
h G4=0/4 62 + 7 52
Depth, ft
Depth, fathoms
Distance, km
Ocean
[1·80]
3·32
6·51
7·11
7·92
Depth, km

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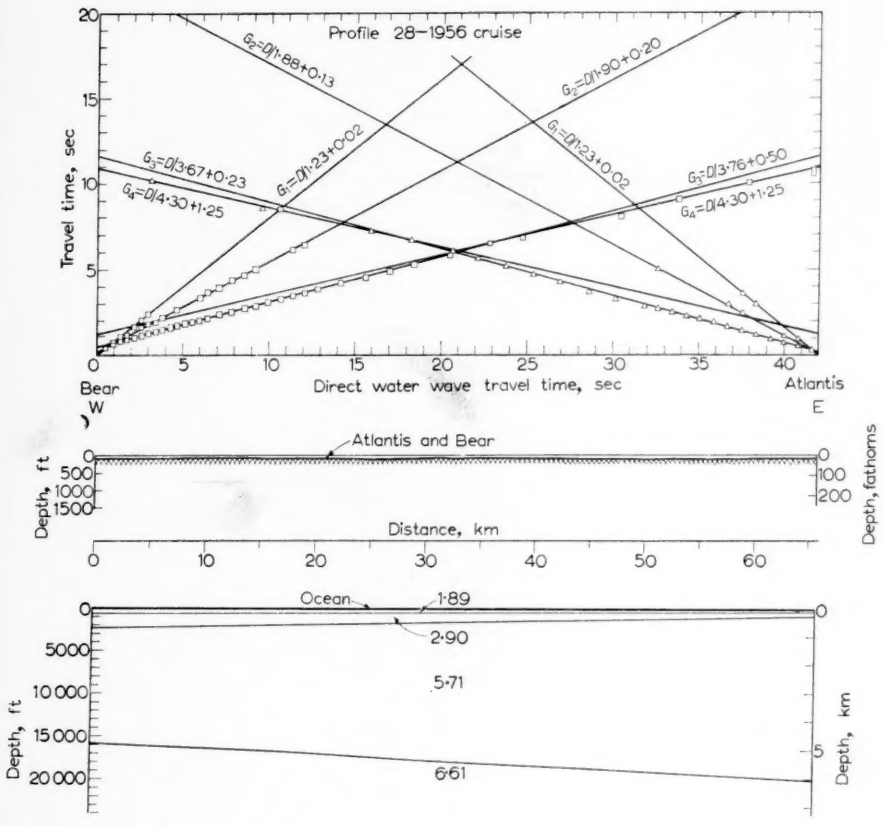
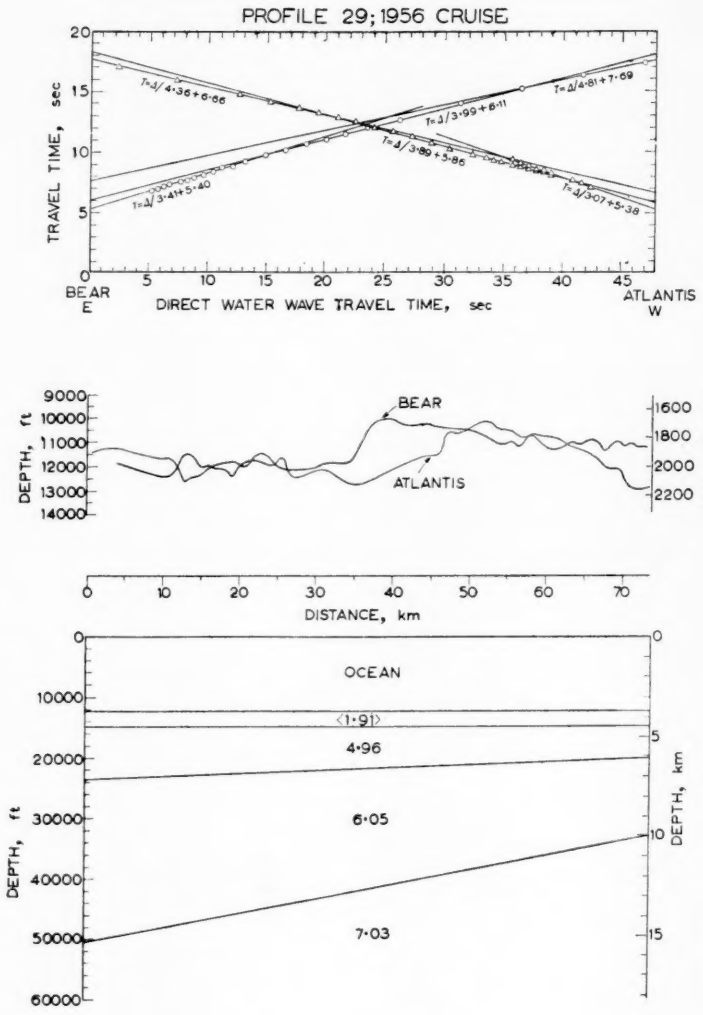

Profile 28–1956 cruise
G_2=0/1·88+0·13
G_2=0/1·90+0·20
G_1=0/1·23+0·02
G_1=0/1·23+0·02
G_3=0/3·67+0·23
G_4=0/4·30+1·25
G_3=0/3·76+0·50
G_4=0/4·30+1·25
Travel time, sec
Direct water wave travel time, sec
Bear
W
Atlantis
E
Atlantis and Bear
Depth, ft
Depth, fathoms
Distance, km
Ocean
1·89
2·90
5·71
6·61
Depth, ft
Depth, km


PROFILE 29; 1956 CRUISE
TRAVEL TIME, sec
T=Δ/4·36+6·66
T=Δ/4·81+7·69
T=Δ/3·99+6·11
T=Δ/3·89+5·86
T=Δ/3·41+5·40
T=Δ/3·07+5·38
BEAR E
DIRECT WATER WAVE TRAVEL TIME, sec
ATLANTIS W
DEPTH, ft
BEAR
ATLANTIS
DEPTH, fathoms
DISTANCE, km
OCEAN
⟨1·91⟩
4·96
6·05
7·03
DEPTH, km

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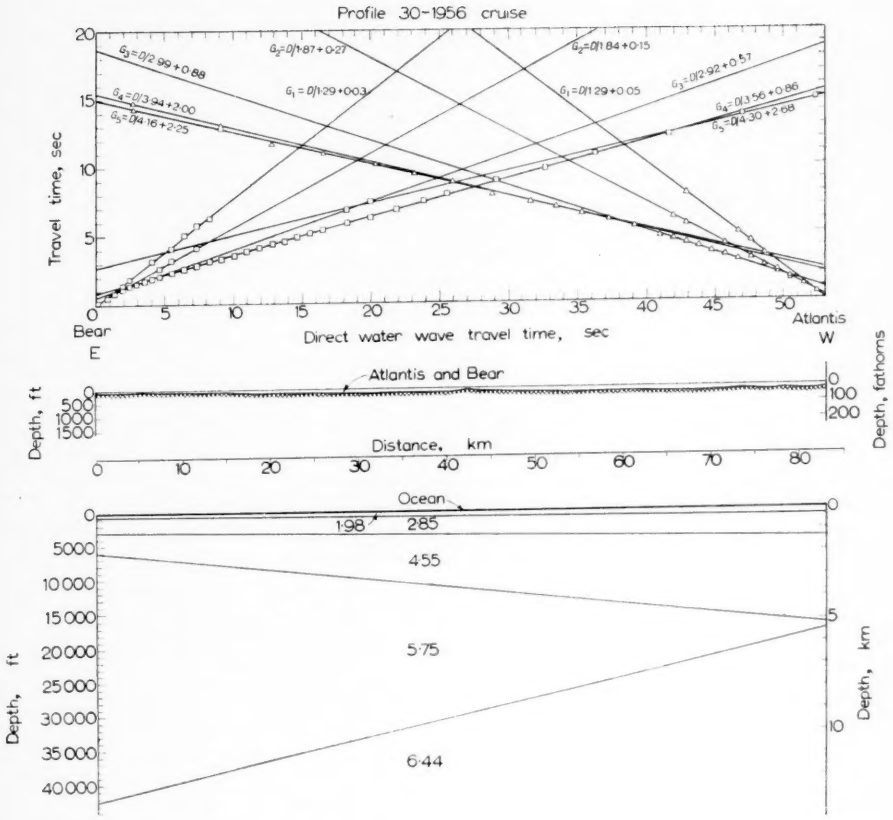
Profile 30-1956 cruise
Travel time, sec
Direct water wave travel time, sec
Bear
E
Atlantis
W
$G_5=0/2\cdot99+0\cdot88$
$G_4=0/3\cdot44+2\cdot00$
$G_3=0/4\cdot16+2\cdot25$
$G_2=0/1\cdot87+0\cdot27$
$G_1=0/1\cdot29+0\cdot03$
$G_2=0/1\cdot84+0\cdot15$
$G_1=0/1\cdot29+0\cdot05$
$G_3=0/2\cdot92+0\cdot57$
$G_4=0/3\cdot56+0\cdot86$
$G_5=0/4\cdot30+2\cdot68$
Atlantis and Bear
Depth, ft
Depth, fathoms
Distance, km
Ocean
1·98
2·85
4·55
5·75
6·44
Depth, ft
Depth, km

on the order of 6·0–6·5 km/sec and one for a velocity of 7·0–7·5 km/sec. This is not entirely consistent, however; and it is usually difficult to tell whether the velocity change from the top to the bottom of the layer is continuous or discontinuous. The Atlantic basin profiles are satisfactorily fit with a single crustal line.

This section shows the contrast in structure going from the interior basin of the Caribbean across the arc to the Atlantic basin. Probably the most noticeable change is between the greatly thickened crust under the Aves swell and the island arc and the comparatively thin crust under the Puerto Rico trench. Also the sharp change in depth to the high velocity crustal layer between Barbuda and profile *6* is striking. The southwestward dip of the high velocity layers here, although possibly interpretable in some other way, strongly suggests an overthrust of the Caribbean crust onto the oceanic crust. The depression of the higher velocity, denser layers provides an explanation of the negative gravity anomaly belt whose axis is approximately coincident with profile *7*.

The material constituting the upper layers in this section is difficult to identify specifically from seismic velocity alone. In general the profiles have not been located to allow a tie-in with detailed land geology; but from the work of the several investigators listed in the references, we have a general knowledge of the variety of sedimentary, metamorphic, volcanic, and igneous rocks present. It has been the primary aim of these seismic investigations to study the broader, more general features of island arc structure; hence we will not attempt to identify each layer as a specific geologic bed, such being considered somewhat speculative from the existing data. The upper layer (stipples) has velocities which are associated with unconsolidated and with slightly lithified sediments. The next two deeper layers (diagonals and hachures) have velocities characteristic of many sedimentary, igneous, and metamorphic rocks, the lower velocities being more characteristic of sedimentary and volcanic rocks and the higher velocities of igneous and metamorphic rocks. The high velocity crustal layers (checks) have been most often identified as basic igneous in composition. In the present case it seems quite possible that the upper part, which tends to lower velocities, may be more acidic than normal oceanic crustal composition. The deepest layer (verticals), with a velocity of about 8 km/sec or higher, is identified as the mantle. The mantle material is considered to be ultrabasic in composition.

In general, on nearby profiles, the hachured layer correlates with the igneous basement complex of the islands. The diagonalled layer correlates with the volcanic, detrital sedimentary, and reef limestone rocks. The stippled layer correlates with the sediment.

There is a discrepancy in the results of profiles *5* and *6* and profile *17*, possibly due to the difference in the direction of the shooting but more likely due to navigation. In this area the depths are changing rapidly and a relatively small error in navigation could produce the disagreement. The structure section has been drawn using the average values from these profiles.

Section 2

Section 2, shown in Fig. 15, begins on the Aves swell and continues north along its axis, crosses the inner volcanic arc of the Lesser Antilles at St. Eustatius and outer arc at St. Barthelemy, and continues across the Puerto Rico trench out to

VOL.
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959

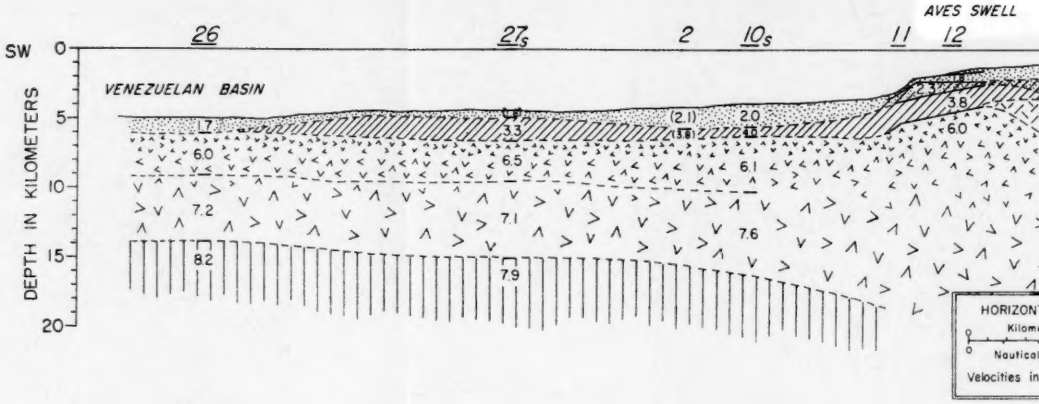

AVES SWELL
SW
26
27s
2
10s
11
12
VENEZUELAN BASIN
DEPTH IN KILOMETERS
0
5
10
15
20
1.7
3.3
(2.1)
(1.6)
2.0
1.2
3.8
6.0
6.0
6.5
6.1
7.2
7.1
7.6
8.2
7.9
HORIZON
Kilom
Nautical
Velocities in

Fig. 14

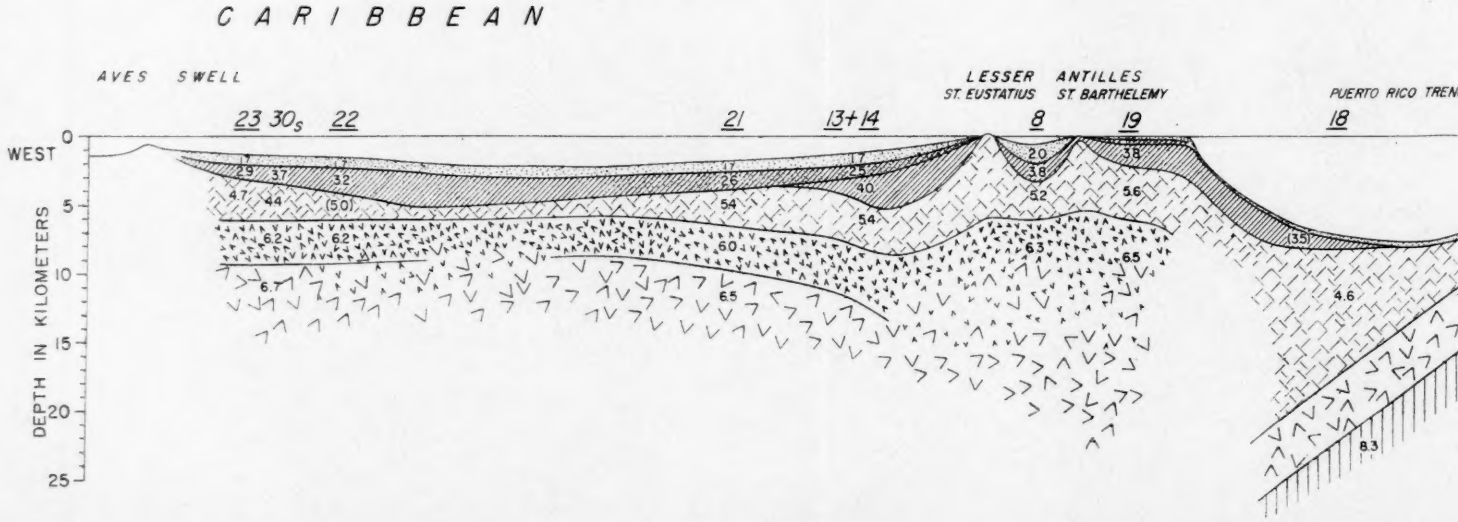

CARIBBEAN
AVES SWELL
LESSER ANTILLES
ST. EUSTATIUS
ST. BARTHELEMY
PUERTO RICO TREN
23
30s
22
21
13+14
8
19
18
WEST
DEPTH IN KILOMETERS
0
5
10
15
20
25
1.7
2.9
3.7
3.2
4.7
4.4
(5.0)
6.2
6.2
6.7
1.7
2.6
2.5
4.0
5.4
5.4
6.0
6.5
2.0
3.8
5.2
3.8
5.6
6.3
6.5
(3.5)
4.6
8.3

Fig. 15

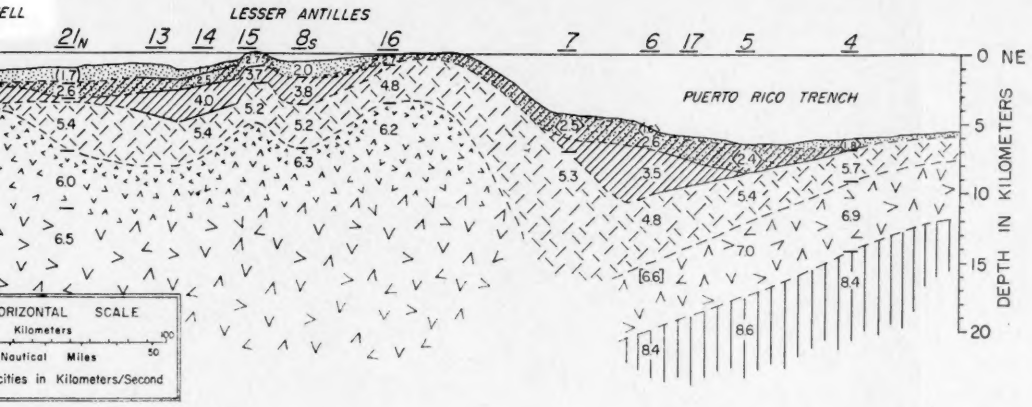


Fig. 14

A T L A N T I C

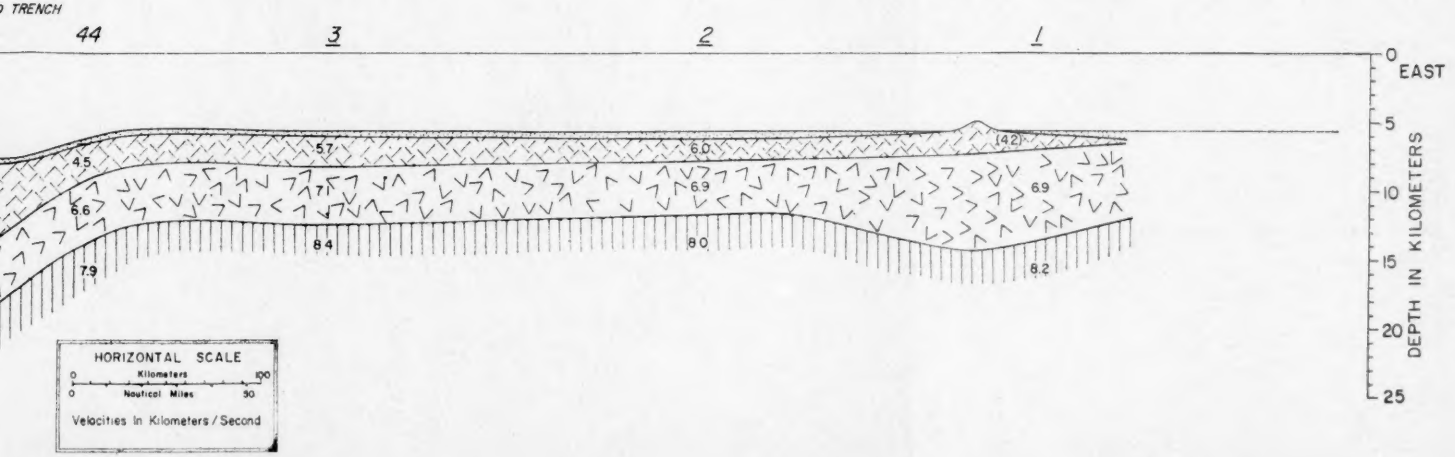
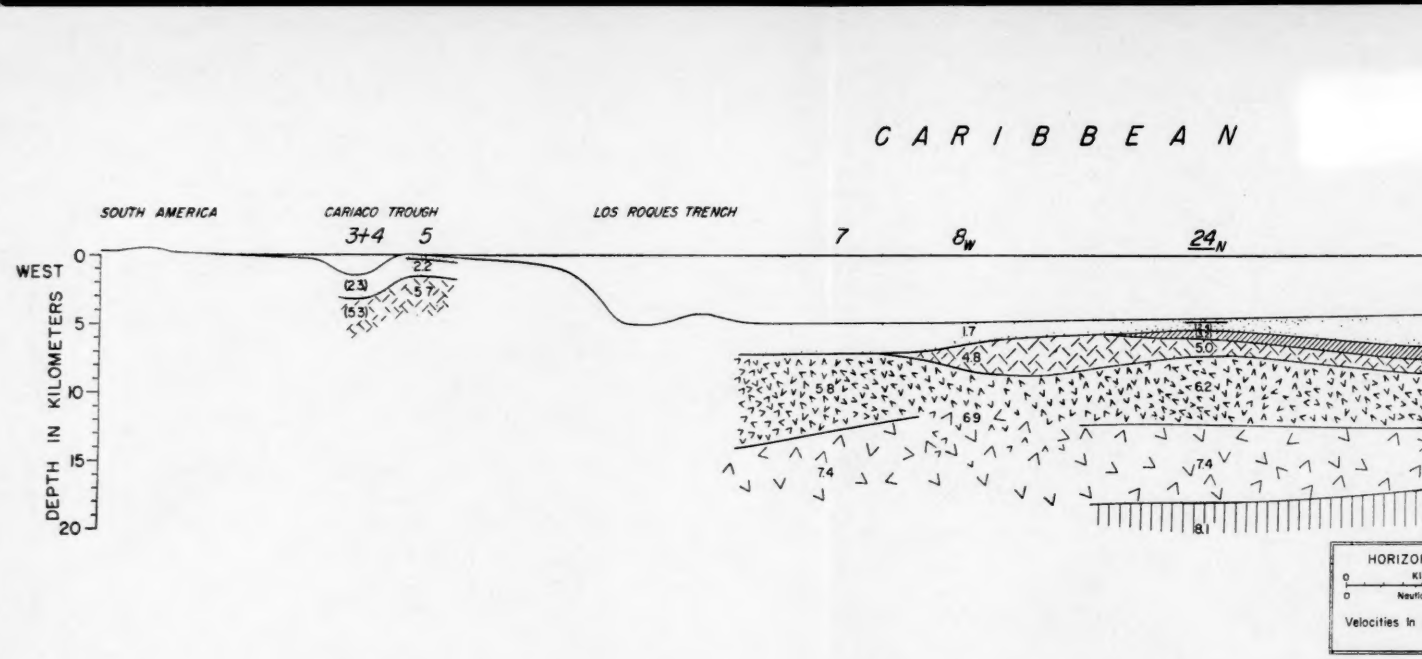
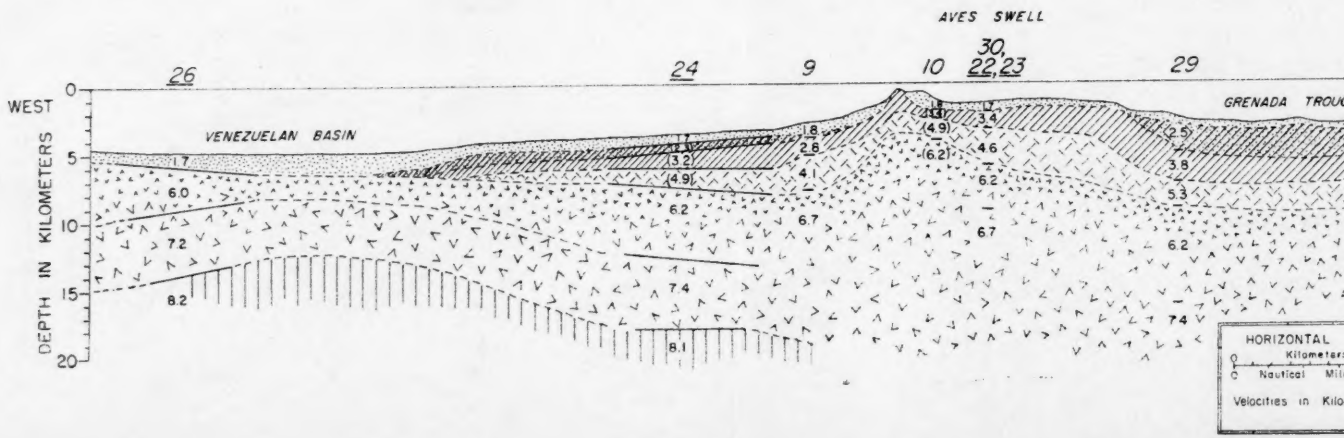


Fig. 15


CARIBBEAN
SOUTH AMERICA
CARIACO TROUGH
LOS ROQUES TRENCH
3+4
5
7
8w
24N
WEST
DEPTH IN KILOMETERS
0
5
10
15
20
2.2
(2.3)
(5.3)
5.7
1.7
4.8
5.8
6.9
7.4
5.0
6.2
7.4
8.1
HORIZON
Velocities in

Fig


AVES SWELL
26
24
9
10
30,
22,23
29
WEST
DEPTH IN KILOMETERS
VENEZUELAN BASIN
GRENADA TROU
0
5
10
15
20
1.7
6.0
7.2
8.2
1.8
2.6
(3.2)
(4.9)
4.1
6.2
6.7
7.4
8.1
3.4
(4.9)
(6.2)
4.6
6.2
6.7
(2.5)
3.8
5.3
6.2
7.4
HORIZONTAL
Kilometers
Nautical
Velocities in Kilo

Fig

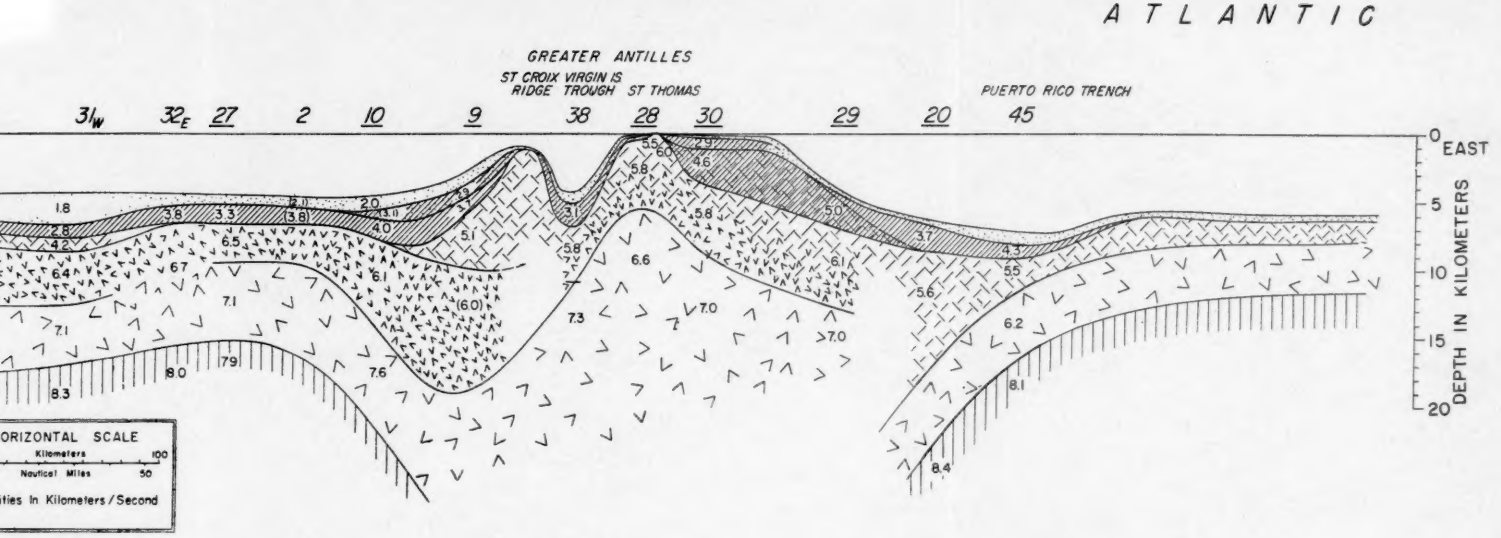

ATLANTIC
GREATER ANTILLES
ST CROIX VIRGIN IS
RIDGE TROUGH ST THOMAS
PUERTO RICO TRENCH
31W 32E 27 2 10 9 38 28 30 29 20 45
0
5
10
15
20
EAST
DEPTH IN KILOMETERS
ORIZONTAL SCALE
Kilometers 100
Nautical Miles 50
ities In Kilometers / Second

Fig. 16

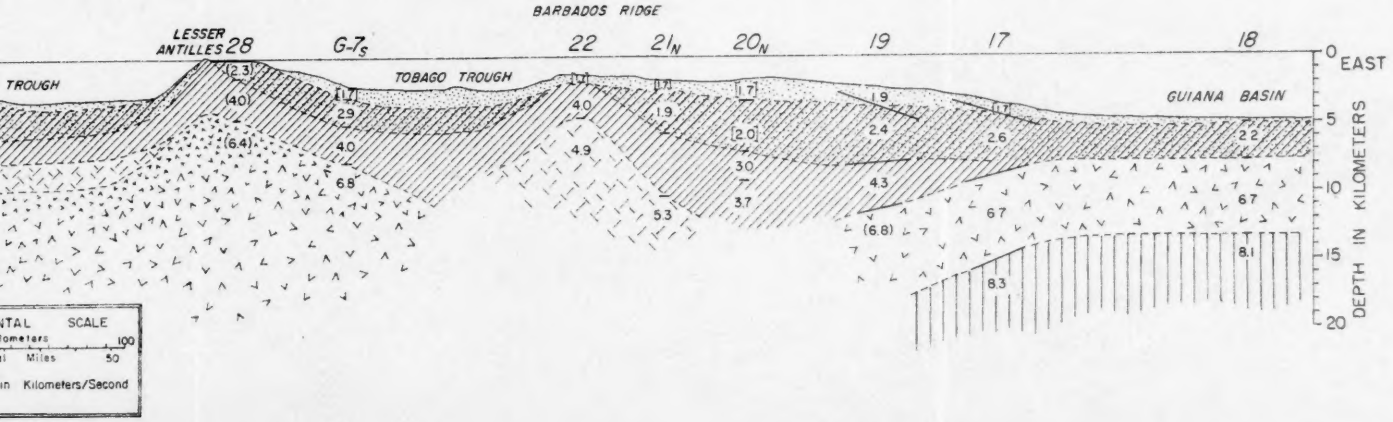

BARBADOS RIDGE
LESSER ANTILLES
28 G-7S 22 21N 20N 19 17 18
TROUGH
TOBAGO TROUGH
GUIANA BASIN
0
5
10
15
20
EAST
DEPTH IN KILOMETERS
NTAL SCALE
ometers 100
l Miles 50
n Kilometers/Second

Fig. 17

VOL.
3
195

the Atlantic basin. The section is about 700 miles long and includes the data from thirteen profiles.

As is valid for the other sections, the seismic velocities and their associated layering can be separated conveniently into the five groups shown. The vertical lines designate mantle material. The checks designate crustal material. The hachures designate material with seismic velocities somewhat lower than those normally associated with the suboceanic crust; the velocities are characteristic of many metamorphic and igneous intrusive rocks. The diagonals designate a group whose velocities are characteristic of many sedimentary and volcanic rocks. The stipples designate unconsolidated and partially lithified sediments.

The mantle was reached only on profiles *1*, *2*, *3*, 44, and *18* in the Atlantic basin and Puerto Rico trench. None of the Lesser Antilles or Aves swell stations measured the Mohorovicic discontinuity. As with Section 1, there is a conspicuous difference between the crust of the Lesser Antilles and that of the Atlantic basin and Puerto Rico trench. The crust in the latter area is fairly uniform with a thickness of 4–5 km and a velocity of 6·6–7·1 km/sec. Beneath the Lesser Antilles and Aves swell the crust is considerably thicker and more variable in configuration and velocity composition. Two crustal layers are observed. The upper crustal layer has a lower seismic velocity than that normally associated with an oceanic crust, suggestive of a somewhat more acidic composition.

The abrupt change in the deep structure across the slope from the Lesser Antilles to the Puerto Rico trench is conspicuous on this section. The thickened and lower velocity crustal section of the Caribbean suggests that the primary mechanism in its development has been the introduction of a differentiate of lighter material from deep in the mantle into the upper mantle and crustal layers. The abrupt change in configuration at the edge of the Caribbean suggests that a second mechanism of importance has been an overthrusting along a major fracture zone of the island arc portion of the Caribbean onto the Puerto Rico trench portion of the Atlantic. The force for such a deformation is presumed to be a horizontal compression, probably associated with the introduction of the differentiate material in the Caribbean. The geometry and elementary mechanics for such a configuration have been given by GUNN (1947).

Section 3

Section 3, shown in Fig. 16, begins on the north coast of Venezuela, crosses the Cariaco trough and the westward extension of the Lesser Antilles north of South America, crosses the Los Rocques trench and continues along the Venezuelan basin near its boundary with the Aves swell, crosses the Greater Antilles island arc at the St. Croix ridge, Virgin Island trough, Island of St. Thomas, and shelf north of St. Thomas, and continues across the Puerto Rico trench out to the Atlantic basin. The section is about 750 miles long and includes the data from eighteen profiles.

The mantle was reached on profiles *24*, 31, 32, and *27* in the Caribbean and on profiles *20* and 45 in the Atlantic. The depth to the Mohorovicic discontinuity averages 17 km in the Caribbean and 12 km in the Atlantic. The Caribbean section shows, as before, a thick crust variable in configuration and velocity composition as compared with the Atlantic basin crust.

The island arc portion, here across the Greater Antilles, is different from that

shown on the section across the Lesser Antilles. From the seismic velocities it is difficult, if not impossible, to distinguish the upper crustal portion from the next overlying layer (hachures). On Section 2 the velocity of this layer averages 5·4 km/sec; here the velocity is 5·8 km/sec. The underlying crustal velocities are also higher than those on the adjacent Lesser Antilles sections. From surface geology the Greater Antilles are presumed to be older than the Lesser Antilles; their geologic development has taken place over a longer period of time than that of the Lesser Antilles. From this it is suggested that these measured velocity differences, higher velocities under the Greater Antilles than those at corresponding depth under the Lesser Antilles, could have occurred and would be an expected result of later stage intrusion and metamorphism.

It should be noted, also, that the change in the deep structure across the slope from the island arc to the trench is not as great here as it is in Sections 1 and 2 across the Lesser Antilles. There is more similarity here between the configuration underlying the northern and southern slopes from the island arc than on the other sections.

Section 4

Section 4, shown in Fig. 17, begins near the middle of the Venezuelan basin and crosses the Aves swell, Grenada trough, Lesser Antilles arc, Tobago trough, Barbados ridge and ends in the western edge of the Guiana basin about 200 miles east of Barbados. This section is 720 miles long and includes the data from fifteen profiles. With a few exceptions the measured velocities can be separated into general groups represented by the five layers in the cross-section.

The entire crustal section was measured at profiles *24* and *26* in the Venezuelan basin and profiles 17 and 18 in the Guiana basin. The mantle was not detectable by any of the other profiles along this section, presumably because it was at too great a depth. The high velocity crustal rocks vary in velocity between 6·0 and 7·4 km/sec. This layer has a wider range of velocities and is thicker in the Caribbean than in the Atlantic. The high velocity crust is thickest and reaches its highest elevation under the Aves swell and the Lesser Antilles arc. Its upper surface is deepest underneath the Barbados ridge. Although it was not detected under the central portion of the ridge, this layer, by extrapolation and by minimum depth computations, appears to be at least 13–14 km deep. Thus the configuration of the high velocity crustal layer and the mantle in this section is much like that in Sections 1, 2, and 4 which cross the Puerto Rico trench. However, the down-thrust or down buckle under the Barbados ridge is much broader than that under the Puerto Rico trench and has a greater sedimentary fill, presumably owing to its proximity to the continent and a good source of sedimentary material. The structure of the Barbados ridge is significantly different from the ridges forming the Aves swell and the Lesser Antilles. The Barbados ridge is composed of the intermediate velocity, derived materials which themselves lie in the trough of the down buckled high velocity layers. The Barbados ridge and the thick sequence of derived material are coincident with the negative anomaly axis (local isostatic or Bouguer). The thick sequence of derived material provides the explanation for the negative anomaly axis. It is surmised that the ridge itself was formed as a result of readjustment of stresses in the crust and mantle toward a more local isostatic equilibrium.

The overlying material, comprising the three upper layers, has velocities

varying from 1·7 to 5·4 km/sec. There is considerable difficulty in correlating these layers throughout the section, understandably so since many volcanic, metamorphic, igneous intrusive, and sedimentary rocks could be included in this velocity range and are probably present in the area. For example, in one place a velocity of 4 km/sec. may represent limestone, and in another it may represent volcanic or metamorphic rock. The greatest thickness of these materials is in the Barbados ridge, where up to 10 km, and possibly much more, is found. In general the profiles on the Barbados ridge are more complicated than usual, with strong dips, faults, and folds. The upper layers (stippled) are probably sedimentary. The large thickness in the Tobago trough and east of the Barbados ridge suggests that the Orinoco river and perhaps the rivers of the Guianas have been major sources of these sediments.

Section 5

Section 5, Fig. 18, crosses the northern end of the Lesser Antilles. To the south of the section is Saba bank. To the northwest is Sombrero, part of the

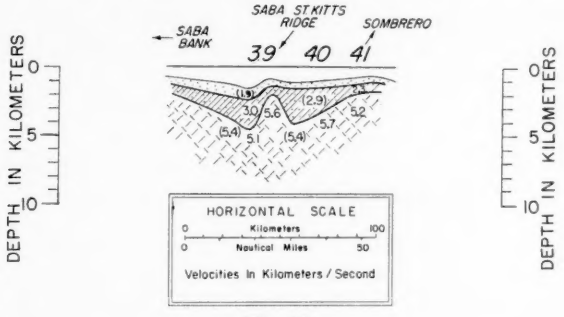


Fig. 18

the outer and older line of limestone-capped volcanoes. This line extends down from Sombrero to Anguilla, St. Martin, Barbuda, Antigua, Grande Terre, and Marie Galente. To the south-east of the central portion of the section are Saba and St. Kitts, part of the inner and younger line of volcanoes. This line extends down from Saba and St. Kitts to Montserrat, Guadaloupe, Dominica, Martinique, St. Lucia, St. Vincent, the Grenadine islands, and Grenada. The structure cross section shows the subsurface extension of the Saba–St. Kitts ridge. This extension is indicated in the surface topography but is more pronounced across the buried ridge itself.

Section 6

Section 6, Fig. 19, crosses the southern slope of Puerto Rico. A rather large thickness of sedimentary rock (diagonals and stipples) is measured above the high velocity, crystalline basement (hachures) under the slope. This thick sediment correlates with coastal plain sediments of Miocene and Oligocene age on the south coast of Puerto Rico; the basement correlates with the folded Cretaceous shales and igneous basement complex of Puerto Rico. This entire sequence of sedimentary rock, 12,000–14,000 ft thick, is then presumed to be of Tertiary age. This type of sedimentary development does exist for many other

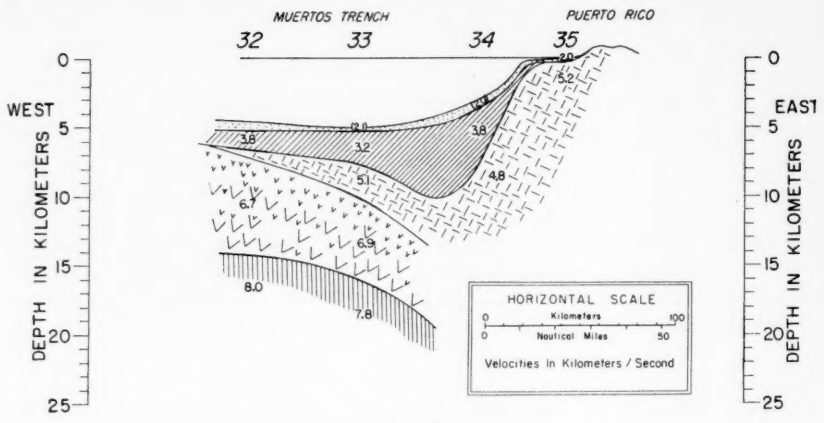


Fig. 19

localities where the adjacent land mass has remained high; it seems likely that this process is one of the more important ones in the continued outward growth of the land-mass areas.

Section 7

This section, shown in Fig. 20, runs south-east from St. Lucia along the ridge which forms the northern boundary of the Tobago trough. Correlation of the

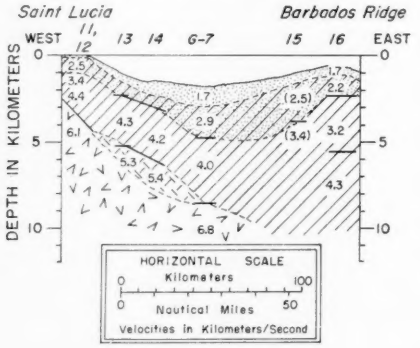


Fig. 20

deeper layers is uncertain, and the reader may prefer a different interpretation from the one shown here. The highest velocity measured was 6·0–6·3 km/sec at profiles 11 and 12 very near St. Lucia. The shot lines at these profiles were relatively short and probably do not give an accurate determination of the velocity in the deepest layer. If the velocities were somewhat lower, they might be correlated with the 5·3 km/sec layer found in profiles 13 and 14, in which the 6 km/sec material would be deeper than has been shown. However, the fact that the highest velocity at profiles 11 and 12, although poorly determined, does appear to be 6 km/sec or higher and the fact that no 5·3 km/sec layer was

found at profiles G7 (26, previous stations) or 28 gave preference to the interpretation we have shown in Fig. 20.

Section 8

Section 8, Fig. 21, runs north–south between Trinidad and Grenada utilizing the data from six profiles. The large syncline shown in the middle of the section is not positively determined, but there is good evidence that the high velocity layer is much deeper there than at either end. Profile 27, located about midway

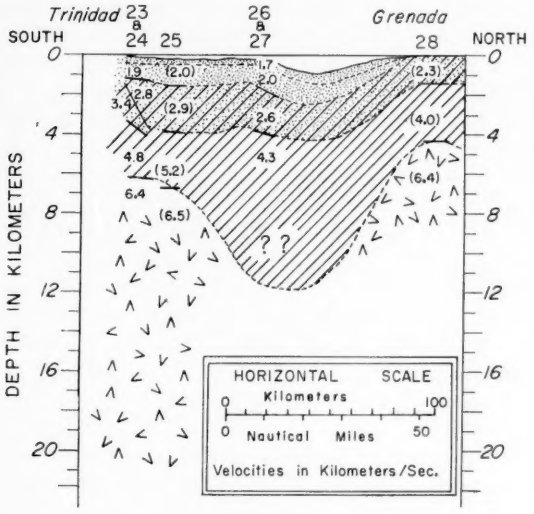


Fig. 21

along the section, was heavily shot; and no velocity higher than 4·3 km/sec was determined by first arrivals, even by the longest shots which were at a range of about 30 miles. Second arrivals give some indication of a 6·4 km/sec layer at a depth of about 12 km, but the evidence is not good enough to warrant drawing the lines on the travel time graph. However, the failure of the travel time graph to show a break from the 4·3 km/sec layer means that the depth to a high velocity crustal layer must be on the order of that shown. To the right (north) in this section the higher velocity layers rise under the Lesser Antilles arc. To the left (south) they rise similarly under northern Trinidad. The synclinal or downdropped area between is possibly a branch of the main downbuckle under the Barbados ridge.

Near Trinidad the 2·3–2·9 km/sec sedimentary layer almost pinches out on profile 24, as both the 3·4 km/sec layer and the 4·8–5·2 km/sec layers slope up rather sharply southward. These upward sloping layers are probably the northern flank of the Northern Coast range of Trinidad and Venezuela. An alternate interpretation of profiles 23 and 24 is possible which could combine the thickness now constituted by the 3·4 km/sec layer and the 2·7 km/sec layer into a single layer with a velocity of about 2·9 km/sec. In either case the depth to the high velocity crustal layer is about the same.

Profile 25 was long and heavily shot, producing strong arrivals through the 6·5 km/sec layer out to a range of 100 km. From this the minimum depth to the mantle was computed to be 21 km, a reasonable depth near the edge of a continent.

CONCLUSIONS ON THE ORIGIN AND DEVELOPMENT OF THE EASTERN CARIBBEAN

Except for the Cayman trough in the northwestern part, the deepest water found inside the island arc of the Caribbean is in the Venezuelan basin. A broad area, approximately between latitudes 12° and 17° north and longitudes 66° and 70° west, is deeper than 2500 fathoms; and in some places the depth is greater than 2900 fathoms. In view of the fact that the water depth is nearly as great as that in ocean basins, it was expected that the measurements would show the crustal structure to be similar to oceanic. The average oceanic structure is 5 km of water, 1 km of low velocity sediments, and 5 km of crustal rocks (velocity about 6·5 km/sec) overlying the mantle (velocity about 8·1 km/sec), e.g. OFFICER *et al.* (1952), M. EWING *et al.* (1954), KATZ and M. EWING (1956), RAITT (1956), and J. I. EWING and M. EWING (in press).

Indeed, the structure, particularly in the deepest part, was found to be similar to oceanic structure; however there were significant differences. In particular, the high velocity crustal rock is not included in a single layer with the same velocity throughout as in an oceanic section, but instead is constituted such that the lower part has an appreciably higher velocity than the upper part. It is difficult to say whether the crust is composed of two distinct layers, implying two types of material, or whether there is a velocity gradient which, due to scatter in the travel time graph, is interpreted as a discontinuous change in velocity rather than a continuous change. In addition, the crustal materials are thicker in general than the normal oceanic crust and thicken appreciably out from the central portion of the basin. Further, the lower velocity materials (1·7–5·5 km/sec) overlying the crust are thicker here than in the Atlantic basin.

At stations *24*, *25*, *26*, and 32 a velocity was measured which can positively be associated with the mantle. At these stations the velocity is greater than 8 km/sec. At stations *27* and 33 the velocity below the deep discontinuity is 7·8–7·9 km/sec, which can probably be associated with the mantle; but the slightly lower than normal velocity suggests that contamination, differentiation or some other process has altered the normal mantle material. The deviation from a standard oceanic structure is even more pronounced at stations 7, *10*, and 29. At these stations, which are in shallower water around the edge of the basin, the highest velocity measured is between 7·0 and 7·6 km/sec. Since all of the profiles discussed here were of about the same length, there is no doubt that the depth to mantle velocity is appreciably less in the deeper areas of the basin than around the edges, as might be expected from isostatic considerations.

In the elevated regions, such as the Aves swell, the depth to mantle by extrapolation is on the order of 20–25 km. Along the island arc the depth is probably

* At many of the stations in the Pacific reported by Raitt, an additional layer with velocity about 5 km/sec is found. The reason that this layer is not generally found on *Atlantis* stations may be that it is masked by a greater thickness of sediment. It is observed, however, on Atlantic basin profiles *1*, *2*, and *3*, as shown in cross-section 2.

near that found under the continental coastal plains. EWING and WORZEL (1954) have computed a depth of 20 km under Puerto Rico from gravity and seismic measurements. The velocities in the various layers of these elevated regions cover a wide range. Aside from the low velocity sediments, the layers range in velocity from 3–4 km/sec in the upper part to about 6·5 km/sec deeper in the crust. In view of the results from the other stations there is a strong likelihood that at the deeper levels the intermediate velocities 7·0–7·6 km/sec would be found between the material which is primarily crustal and that which is primarily mantle.

In previous papers dealing with the Caribbean (OFFICER *et al.*, 1957; EWING *et al.*, 1957), it has been pointed out that the Venezuelan basin structure differs from typical oceanic structure in having a thicker crust, a wider range in crustal velocities, and a lower velocity beneath the deepest discontinuity. It was interpreted that the Caribbean was formerly an oceanic area which has been altered, throughout geologic time. It was surmised that this alteration had occurred principally through the introduction of material from depth in the mantle. The new results can be interpreted similarly. The results at stations *25* and *26* showing that the mantle is only slightly deeper than under the ocean basins leaves little possibility that the Caribbean could have been created by the foundering of a segment of a continent. If this area was formerly a continent, it must have been uplifted 25–30 km, eroded down to sea-level, then submerged about 5–6 km, and overlain by up to 2·5 km of sediments. On the other hand, if it is allowed that the structure was originally oceanic, the main requirements are the addition of large amounts of crustal material, particularly along the island arc and on the Aves swell. It is considered that this would produce the observed effects, namely a thicker crust, a wider range in crustal velocities (both higher and lower than average oceanic crustal velocity), a more gradual change from crustal to mantle velocity, and a greater thickness of derived materials overlying the crust.

As mentioned earlier, a major difference in an oceanic section and a Caribbean section is that in the former there appears to be an abrupt change in velocity from about 6·5 to 8·1 km/sec at the crust-mantle boundary, whereas in the latter we usually find material whose velocity is 7·1–7·7 km/sec between the mantle and the 6·5 km/sec crustal material. In addition, the average Caribbean crust is thicker and usually has lower velocities in the upper part than does the oceanic crust.

If it were simply a question of explaining the presence of an intermediate velocity material between the mantle and crust, a possible approach might be to assume that the Mohorovicic discontinuity is the level about which the pressure and temperature effects produce a change of state in a material whose chemical constitution is about the same above and below. Under these circumstances in an active region like the Caribbean, a relatively thick section of intermediate composition material might have been created. Another possible process for the formation of this intermediate velocity material is the partial serpentinization of peridotite as suggested by HESS (1954). However, neither of these processes by itself would explain the other observed features. From the earlier work in the Caribbean it was suggested (OFFICER *et al.*, 1957), (EWING *et al.*, 1957) that the entire area has been extensively intruded by a differentiate migrating upward from deep in the mantle, and that the raised portions—island arcs and submarine

ridges—were the areas where most of the material reached the surface, and further that the deep sea-trench was the result of the expanded Caribbean crust having been overthrust onto the oceanic crust. This overthrust has depressed the high velocity layers on the oceanic side of the arc creating the deep sea trench and the associated negative anomaly belt. These views still seem to be the most logical ones in the light of the additional data provided by the 1956 cruise. In particular, the stations outside the island arc give even more convincing evidence than the earlier work that the high velocity crustal layer and the mantle dip steeply underneath the arc (Figs. 14, 15 and 16). The additional measurements on the island arc and on the Aves swell show in more detail the greatly thickened crustal section, the velocity increasing with depth in the section, and the presence throughout these areas of much material with velocities characteristic of extrusive and intrusive igneous rock. All of these features are considered to be evidence in favour of the hypothesis that the primary mechanism in the formation of the eastern Caribbean, and presumably other such features, has been the introduction into the upper mantle and crustal layers of a differentiate of lighter material rising from depth in the mantle.

In formulating the ideas presented here we have found among others the following references particularly useful, BUCHER (1950), GUNN (1936, 1937, 1947, 1949), HESS (1938), LAWSON (1932), POLDERVAART (1955), STILLE (1955), TILLEY (1950) and WATERS (1955). Descriptions of the pertinent geology of the Antilles are given in BUTTERLIN (1956), CHRISTMAN (1953), DAVIS (1926), MAXWELL (1948), MEYERHOFF (1933), SCHUCHERT (1935), and WOODRING (1954).

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Woods Hole Oceanographic Institution Contribution No. 999.
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CONTINENTAL MARGINS AND GEOSYNCLINES: THE EAST COAST OF NORTH AMERICA NORTH OF CAPE HATTERAS

By C. L. DRAKE, M. EWING and G. H. SUTTON

Abstract—Many geophysical measurements, including seismic refraction, gravity, magnetics, and echo soundings, have been made along the continental margin of eastern North America north of Cape Hatteras in the last twenty years. These have revealed the presence of two sedimentary troughs, one under the shelf, the other in deeper water under the continental slope and rise which are separated by a ridge in the basement near the edge of the shelf. The sediments in the shelf trough have been drilled to a depth of 10,000 ft and are of shallow water character. Cores of the upper part of the sediments of the outer trough have revealed features attributed to slumping, sliding, and turbidity current action, and, in part, sediments similar to the graywackes of PETTIJOHN's (1949) classification.

This sedimentary system is quite comparable to the Appalachian system as restored for early Paleozoic time. The sediments of the inner and outer troughs are similar to those of the Appalachian miogeosyncline and eugeosyncline (KAY, 1951), respectively, and the basement ridge resembles the Pre-Cambrian axis which separates these two troughs in the Appalachians. While there is no active volcanism in the outer (eugeosynclinal) trough at the present time, evidence of past volcanism is present in the form of partially buried seamounts with large magnetic anomalies. Conditions in the Appalachian eugeosyncline appear to have been similar with but limited volcanism prior to the beginnings of Taconic activity.

The gravity calculations reveal an abrupt change in depth of the Mohorovicic discontinuity near the edge of the shelf. There is some indication that the boundary between the crust and the mantle in this area is gradational rather than a sharp discontinuity.

The major process necessary to convert the present continental margin into a mountain system is the one which thickens the crust under the outer, or eugeosynclinal trough. Since the miogeosyncline is already based on a crust of continental proportions, its deformation requires only a means of folding and thrusting the surficial sediments. This is but a minor part of the overall tectonic activity.

INTRODUCTION

MUCH of the geologic nomenclature is inexact and a particular term may have different meaning or a different shading of meaning for different persons. This is due in part to original definitions which have proved to be too generalized, and in part to distortions of the original meaning. In order that difficulties may not arise from this source, it is worthwhile, at the outset, to state the manner in which some of these terms are used in this paper.

The term "geosyncline", as used here, refers to the orthogeosynclines of STILLE's (1936, 1941) classification. It implies a linear or arcuate belt marginal to a continental shield or craton.

"Orthogeosynclines were classified as eugeosynclines ('straight' or 'real' geosynclines) and miogeosynclines ('lesser geosynclines') by STILLE (1941, p. 15), who used the term quite informally, but clearly implied a volcanic basis of distinction. An eugeosyncline is a surface that has subsided deeply in a belt having active volcanism, a miogeosyncline in a belt lacking active volcanism." (KAY, 1951, p. 4.)

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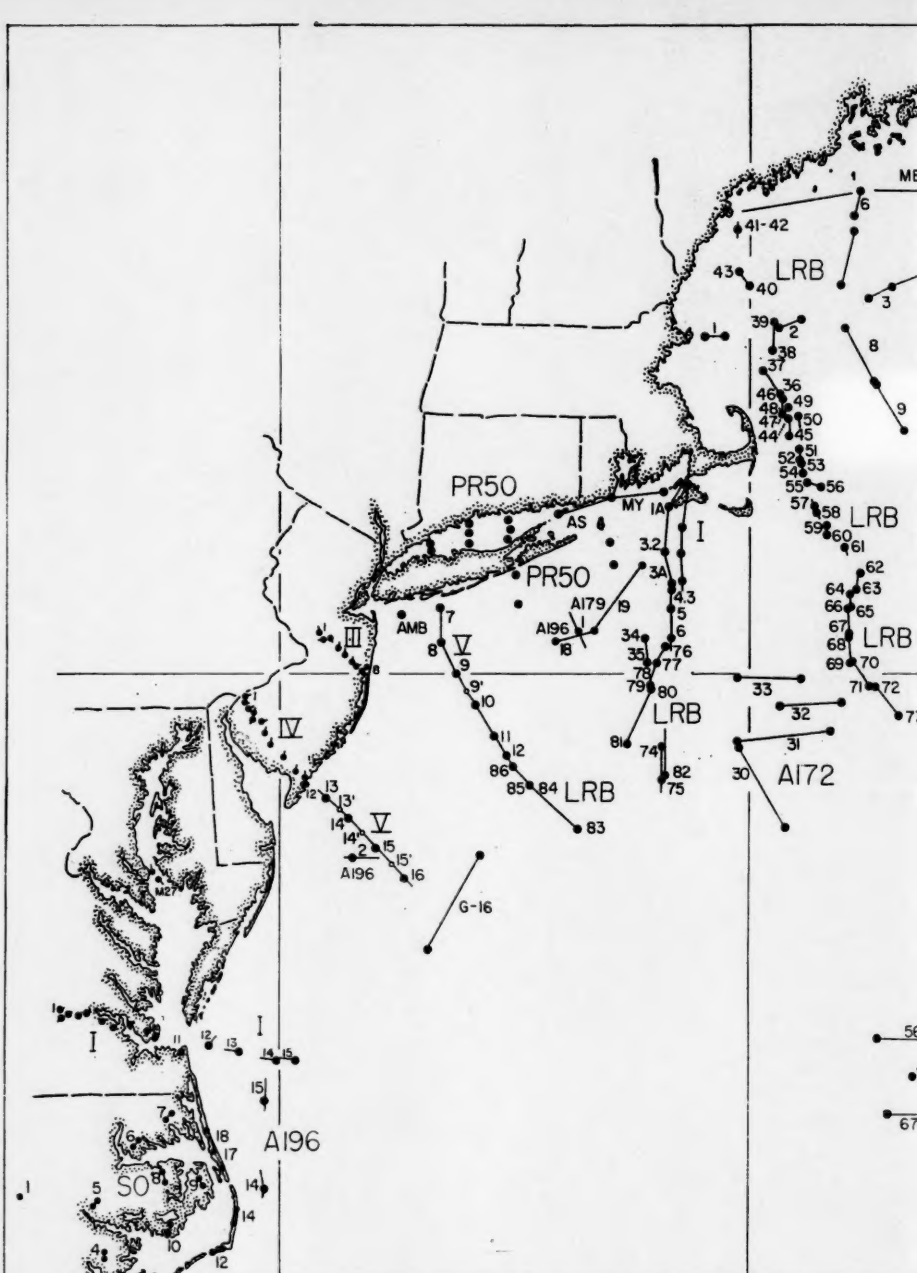
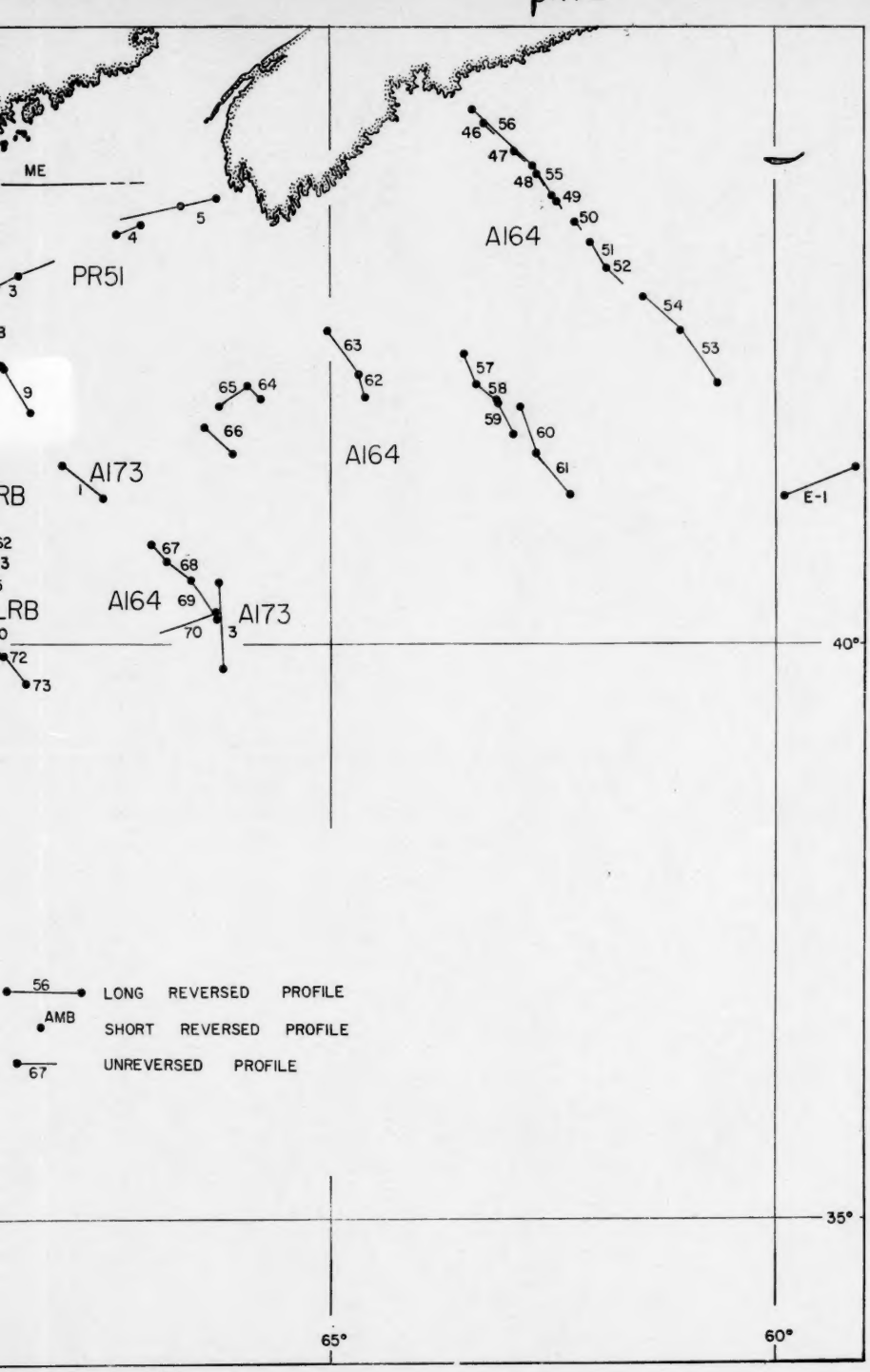


Fig. 1. Location map,



map, seismic stations.

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References to the Appalachian system include both the metamorphic and plutonic belt as well as the folded and thrust-faulted belt to the west. The former is termed the Appalachian eugeosyncline, the latter the Appalachian miogeosyncline following KAY (1951).

In identifying certain of the sediments as "graywackes", the definition given by PETTIJOHN (1949, p. 942–943) is used. The term has been defined in many ways and applied to sediments of different descriptions but the above definition is best suited for the discussions in this paper.

The terminology used for the seismically determined layers within the earth is explained in some detail in a later section. The sedimentary layers are in general discussed as a unit, since their relation to the stratigraphy is not constant. Crustal rocks are those above the Mohorovicic discontinuity and the region below this discontinuity is referred to as the mantle. This is the nomenclature usually used in seismic investigations although "crust" and "mantle" have been used differently in other work. The continental crustal rocks are referred to as "basement", in many cases, for the sake of brevity. This is not in conflict with the general geological use of this term.

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The discussion of the seismic results uses the terminology of the other papers dealing with the emerged and submerged Atlantic coastal plain. Seismic *station* refers to the position of a recording vessel, seismic *profile* refers to the data along the line of shots and may include two *stations* if the profile is reversed, and seismic *section* refers to the geologic structure inferred from the data from a single profile or many profiles along a line.

References to "velocity" within any layer indicate compressional wave velocity. The discussion of velocities deals with the compressional velocities except in cases which state that shear wave velocities are being considered. The velocities indicated on the travel time curves are in kilometres per second while the abscissae represent direct water wave travel times in seconds.

Lastly, the descriptions of the basement rocks often have little petrological significance. "Granite" is an especially abused term and may refer to a variety of metamorphic rocks or even, in some cases, to the point at which drilling of a well becomes very difficult.

HISTORICAL BACKGROUND

In 1935 a programme of seismic refraction measurements, supported by the Geological Society of America, was begun on the Atlantic Coastal Plain. Observations were made on two lines: one extending from the Fall line to the 100 fathom curve off Cape Henry, Virginia; the other extending some 50 miles south from Woods Hole, Mass., on the continental shelf. The results of this work were published in the first of the series entitled "Geophysical Investigations in the Emerged and Submerged Atlantic Coastal Plain" (Part I, EWING *et al.*, 1937). The geological implications of the results were discussed in an accompanying paper by Miller (Part II, MILLER, 1937). In 1939 a series of profiles were shot from Princeton to Barnegat Bay, New Jersey (Part III, EWING *et al.*, 1939), followed by a section in southern New Jersey extending from Bridgeton, on the Delaware River, to Avalon, on the Atlantic Coast (Part IV, EWING *et al.*, 1940).

After World War II the programme was resumed with the continued support

of the Geological Society of America. Three lines running from Avalon, New Jersey, Fire Island, New York, and Woods Hole, Mass., to the 100 fathom curve were measured. An 85 ft crash boat furnished by the Watson Laboratories of the U.S. Army Signal Corps was used for much of this work (Part V, EWING *et al.*, 1950). Support was gradually shifted to the Office of Naval Research, the 1948 work extending the Woods Hole and New York lines into deep water and making a new line from Portland, Maine, to the 1500 fathom curve, being supported in part through use of GSA funds and partly by ONR.

The Long Island–Block Island area was examined next (Part VI, OLIVER and DRAKE, 1951) followed by the Nova Scotia area (Part VII, OFFICER and EWING, 1954), the Grand Banks south of Newfoundland (Part VIII, PRESS and BECKMANN, 1954) and the Gulf of Maine (Part IX, DRAKE *et al.*, 1954). The most recent paper reports a profile extending some 300 miles south from Cape St. Mary, Newfoundland (Part X, BENTLEY and WORZEL, 1956).

Scattered profiles observed between 1948 and the present have filled in gaps left by the earlier work. Most of these results are presented here for the first time. The location map (Fig. 1) shows the distribution of the refraction stations.

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ACKNOWLEDGEMENTS

The data upon which this paper is based were taken by many people over a period of some twenty years. These included personnel from Lehigh University, Woods Hole Oceanographic Institution, University of Wisconsin, Princeton University, Hudson Laboratories, and Lamont Geological Observatory of Columbia University. Many of the results have been published previously.

Of the unpublished data, the 1948 refraction work (LRB) extending the Portland, Woods Hole, and New York lines was done by J. L. Worzel, G. R. Hamilton, R. S. Edwards, J. Northrop, E. T. Miller, T. Madden, and D. H. Shurbet. Preliminary results of some of the work of the Woods Hole Oceanographic Institution (A196) were furnished by J. B. Hersey and Elizabeth Bunce. C. R. Bentley, W. C. Beckmann, J. Dorman, J. L. Worzel, D. Warren, P. C. Wuenschel, J. I. Ewing, and B. C. Heezen participated in the seismic programme on *Atlantis* cruises A172 and A173.

Information concerning wells to basement was given by Jasper Stuckey, State Geologist of North Carolina, Meredith Johnson, State Geologist of New Jersey, W. B. Allen of the United States Geological Survey and A. S. Wyner of Ball Associates. General information about the magnetic measurements was given by J. Hirshman and E. T. Miller; information about gravity data by J. L. Worzel. D. Warren kindly furnished preliminary information about the results off Recife, Brazil, and W. Ludwig results from the Argentine shelf. J. L. Kulp and L. Long provided helpful information on radioactive age determinations.

Many others assisted in accumulating the large body of data used in this work and this assistance is gratefully acknowledged. It is impossible to carry out an extensive programme at sea without the willing co-operation of all participants.

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PRINCIPLES OF INTERPRETATION

The method used to interpret the seismic refraction results is, basically, that described in Part III of the series (EWING *et al.*, 1939, pp. 262–268). This method is based on four assumptions:

1. Each layer is bounded top and bottom by planes, and transmits seismic waves at a constant velocity.

2. A wave travelling in any layer with velocity V, and incident upon the surface of the layer at an angle, α with the normal, has an apparent velocity $V/\sin\alpha$ along the surface.

3. At the interface between two layers the path of the seismic wave is bent according to Snell's law, $\sin\alpha_1/\sin\alpha_2 = V_1/V_2$.

4. Any travel time will be unchanged if shot point and recording point are interchanged.

The arrivals from the shots of a particular profile are plotted in the form of travel time curves with travel time of the ground arrival as the ordinate and distance (or direct water wave travel time) as the abscissa. If the assumptions made earlier are correct, then arrivals from any one layer should fall on a straight line segment represented by an equation of the form $t = (x/V_a) + t_a$, where x is the distance, V_a the velocity, and t_a is the time intercept of the line segment extended back to $x = 0$.

If the layers which are being examined are not horizontal the apparent velocities will be greater for shots fired up dip from the recording boat and less for those fired down dip. In order to find the true velocity and the apparent dip along the line of the profile, it is necessary to reverse the profile. The customary procedure is for the shot boat to shoot out in one direction until enough information to define the layers accurately has been obtained. It then heaves to and becomes the receiving boat and the original receiving boat shoots in toward it. This gives two sets of data, one up dip, the other down. These are plotted from opposite ends of the travel time graph with the separation determined by the distance between the receiving positions. By the fourth principle above, the reverse points, the projections of the travel time curves to the reverse ordinates, should be equal.

The dip that is determined will be the apparent dip along the line of the profile and will not equal the true dip unless the profile is shot normal to the strike of the layers. Most of the profiles in this report were shot with this orientation.

A number of practical problems must be considered in applying this method of interpretation to the data. Any particular layer will be represented as first arrivals on a travel time curve for only a portion of the curve. That part of a layer that is represented by first arrivals on the forward half of the profile is not necessarily the same as that represented by the reverse but may be separated by some distance. If good secondary arrivals can be read or if the area is one in which rapid changes in the upper layers are not anticipated, then reversal is justified. If, on the other hand, large changes may be expected, such as in the vicinity of the continental slope, errors may result from forcing a reversal.

Horizontal changes in velocity may be differentiated from changes in slope by reversed profiles provided that the reversed segments are over the same part of the profile and there are enough data. If there is a break in a line segment due to horizontal change in velocity, the "true" velocity derived from the forward and

Table 1. Results of Seismic Refraction Measurements off the East Coast of North America North of Cape Hatteras

1. Station Numbers

These are the same as those on the location map (Fig. 1) with the exception that the cruise numbers have been left out. As the stations are listed by area, they may be easily located on the map.

2. Velocities

These are given in km/sec as is the case on the velocity contour map (Fig. 15). The layer terminology is that described in the text.

3. Thicknesses

The layer thicknesses and water depths are given in kilometres.

4. Depths

The depths are given in kilometres. The depth to the crust is the distance from the surface to the uppermost crustal layer identified. The mantle depth represents the depth to the Mohorovicic discontinuity.

Station	Velocity						Thickness						Depth		Ref.
	Sediment			Crust		Mantle	Water	Sediment			Crust		Crust	Moho	
	Uncon.	Semi.	Cons.	Cont.	Ocean.			Uncon.	Semi.	Cons.	Cont.	Ocean.			
Newfoundland Section															
6S	(1·79)	2·25, 2·66	3·93	—	6·70	7·76	4·88	0·33	2·05	1·95	—	1·37	9·24	10·60	1*
6N							4·39	1·02	1·43	3·38	—	5·11	10·22	15·34	
7S	1·78	2·63	3·84	5·78	7·59	—	4·35	1·27	1·03	2·31	3·26	—	8·99	—	1
7N							4·35	0·69	1·98	3·03	2·89	—	10·05	—	
8S	1·79	2·31	4·14	(5·87)	7·24	—	3·77	0·62	2·75	2·84	1·90	—	9·94	—	1
8N							3·02	0·71	2·12	5·38	1·90	—	11·19	—	
9S	1·84	2·36	3·68	5·97	—	—	2·71	1·04	1·42	6·88	—	—	12·07	—	1
9N							1·81	0·22	1·06	5·50	—	—	8·60	—	

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10S							1·76	0·76	1·34	5·37	—	—	7·47	—	
													8·10		
	1·96	2·60	4·28	5·45	—	—							6·55		1
													4·24		
10N							0·07	0·76	0·57	0·70	—	—	1·96		
16S	1·59	—	4·35	5·55	(6·39)?	—	0·10	0·33	—	1·97	2·85	—	2·41	—	2
16N							0·10	0·03	—	0·93	3·40	—	1·06	—	
Scattered Stations															
Grand Banks, Cabot Strait															
11W	1·78	—	3·69	(5·19,	—	—	0·09	0·72	—	0·88	3·04	—	1·69	—	2
11E				5·81)			0·09	0·72	—	—	—	—	—	—	
12N	1·75	—	(3·38)	4·93,	—	—	0·07	0·48	—	0·21	3·61	—	0·77	—	2
12S				(6·10)			0·07	0·48	—	0·91	2·93	—	1·47	—	
15N	1·77	1·94	4·13	5·29,	—	—	0·08	0·40	0·80	0·41	3·91	—	1·69	—	2
15S				(6·39)			0·08	0·40	0·92	1·95	1·54	—	3·35	—	
17SW	1·74	2·84	4·12	5·29,	—	—	0·06	0·55	1·52	0·74	5·75	—	2·88	—	2
17NE				(6·59)			0·06	0·42	0·46	1·28	5·77	—	2·23	—	
18SW	(1·75)	2·93	3·80	6·08	—	—	0·39	0·44	1·56	1·22	—	—	3·61	—	2
18NE							0·39	0·16	0·52	4·25	—	—	5·01	—	
19SW	1·77	3·16	4·61	—	—	—	0·04	0·81	1·66	—	—	—	—	—	2
19NE							0·04	0·77	1·87	—	—	—	—	—	
North-east end, Georges Bank															
64N	(1·70)	2·81	—	4·89	—	—	0·24	0·52	1·01	—	—	—	1·77	—	3
64S							0·26	0·52	0·93	—	—	—	1·71	—	
65N	1·70	2·67	—	4·66	—	—	0·15	0·51	1·71	—	—	—	2·37	—	3
65S							0·09	0·52	1·48	—	—	—	2·08	—	
66N	1·74	2·61	—	5·10	—	—	0·07	0·35	1·41	—	—	—	1·84	—	3
66S							0·06	0·46	1·51	—	—	—	2·06	—	
Halifax Section															
56N	(1·65)	(2·26)	—	5·72	—	—	0·05	0·02	—	—	—	—	0·06	—	3
56S							0·21	0·34	1·53	—	—	—	2·08	—	
47	1·67	—	—	(4·59)	—	—	0·24	0·18	—	—	—	—	0·41	—	3

* These numbers refer to the reference list appearing at the end of Table 1 on p. 127.

Table 1—continued

Station	Velocity						Thickness						Depth		
	Sediment			Crust		Mantle	Water	Sediment			Crust		Crust	Moho	Ref.
	Uncon.	Semi.	Cons.	Cont.	Ocean.			Uncon.	Semi.	Cons.	Cont.	Ocean.			
Halifax Section—(contd.)															
55N	(1·65)	2·26	—	5·92	—	—	0·22	0·15	1·30	—	—	—	1·66	—	3
55S							0·09	0·17	1·25	—	—	—	1·50	—	
48	(1·65)	(2·76)	—	(5·10)	—	—	0·18	0·36	0·52	—	—	—	1·07	—	3
49	1·62	(2·77)	(3·76)	(5·64)	—	—	0·07	0·46	0·74	1·87	—	—	3·13	—	3
50	1·74	(2·76)	(3·44)	(5·66)	—	—	0·09	0·65	0·50	1·60	—	—	2·84	—	3
51N	1·68	2·48	3·91	(5·60)	—	—	0·10	0·38	0·97	2·91	—	—	4·35	—	3
51S							0·10	0·71	1·00	2·91	—	—	4·72	—	
52	1·65	(2·78)	—	(5·39)	—	—	0·08	0·81	1·86	—	—	—	2·75	—	3
54N	1·80	2·92	—	5·13	—	—	1·17	1·97	2·96	—	—	—	6·10	—	3
54S							3·51	1·96	—	—	—	—	5·46	—	
53N	1·76	—	—	4·52	7·07	—	3·51	1·73	—	—	3·51	—	5·24	—	3
53S							3·97	1·26	—	—	3·51	—	5·24	—	
E-1	1·83	2·05	—	3·97	6·69	8·22	4·79	0·33	1·79	—	3·43	4·34	6·91	14·68	4
Browns Bank Section															
5W	1·53	—	—	4·57, 5·94	—	—	0·12	0·22	—	—	2·99	—	0·34	—	5
63N	1·68, 1·87	2·60	—	5·38	—	—	0·11	0·49, 0·04	1·54	—	—	—	2·17	—	3
63S							0·12	0·35, 0·27	1·38	—	—	—	2·12	—	
62N	(1·71)	(2·74)	—	(5·02)	—	—	—	—	—	—	—	—	—	—	3
62S							2·10	1·07	2·25	—	—	—	5·42	—	
57N	1·71	2·81	—	4·02	—	—	1·81	0·94	2·22	—	—	—	4·96	—	3
57S							2·41	1·23	1·00	—	—	—	4·63	—	

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58N	1·74	(2·10)	—	4·17	—	—	2·38	1·61	0·35	—	—	—	4·33	—	3
58S		(2·77)					2·94	0·37	2·17	—	—	—	5·49	—	
59N	1·74	1·98	—	4·49	—	—	2·94	0·57	2·23	—	—	—	5·73	—	3
59S							3·57	0·08	2·05	—	—	—	5·70	—	
60N	(1·75)	1·95	—	(4·88)	6·91	—	3·31	0·36	2·45	—	2·50	—	6·13	—	3
60S							3·71	0·06	2·45	—	2·53	—	6·22	—	
61N	(1·75)	1·94	—	5·54	7·22	—	3·69	0·33	2·64	—	4·42	—	6·64	—	3
61S							4·28	0·12	2·87	—	2·90	—	7·25	—	
Matinicus—Georges Bank Section															
6N	1·53	—	—	6·03	—	—	0·05	0·05	—	—	—	—	0·10	—	5
6S							0·12	0·04	—	—	—	—	0·15	—	
7N	—	—	4·02	6·01	—	—	0·09	—	—	0	—	—	0·09	—	5
7S							0·15	—	—	0·49	—	—	0·64	—	
8N	—	2·07	—	5·92	—	—	0·16	—	0·12	—	—	—	0·28	—	5
8S							0·21	—	0·10	—	—	—	0·31	—	
9N	—	2·07	—	6·01	—	—	0·19	—	0·05	—	—	—	0·24	—	5
9S							0·22	—	0·31	—	—	—	0·53	—	
1N	1·50	2·92	—	5·63	—	—	0·11	0·60	2·54	—	—	—	3·25	—	6
1S							0·18	0·52	2·03	—	—	—	2·73	—	
67N	1·84	2·60	—	5·02	—	—	0·07	0·41	1·18	—	—	—	1·65	—	3
67S							0·20	0·48	1·03	—	—	—	1·72	—	
68N	1·70	1·94	(2·94)	5·32	—	—	0·32	0·30	0·30	0·32	—	—	1·25	—	3
68S							1·06	0·42	0·30	4·10	—	—	5·88	—	
69N	1·74	2·10	3·28	5·00	6·89	—	1·99	0·58	0·30	1·76	—	—	4·63	—	3
69S							2·18	0·30	0·87	2·02	2·60	—	5·36	—	
70	1·68	(2·10)	(3·28)	(4·78)	(6·60)	(8·48)	2·76	0·41	1·16	1·70	3·30	—	6·04	—	3
3N	1·74	—	3·86	—	6·60	—	2·77	0·41	1·16	1·60	2·10	7·85	5·94	15·90	6
3S							2·76	2·75	—	2·69	—	—	5·51	—	
Portland, Maine, Section							3·53	1·02	—	2·67	—	—	4·55	—	
41–42	1·59	—	—	5·49	—	—	0·05	0·02	—	—	—	—	0·07	—	5
40	1·59	—	—	4·82,	—	—	0·05	0·15	—	—	0·57	—	0·20	—	5
43				5·91			0·05	0·15	—	—	0·19	—	0·20	—	
39	1·71	—	—	5·70	—	—	0·27	0·10	—	—	—	—	0·37	—	5
38							0·28	0·13	—	—	—	—	0·42	—	

Table 1—continued

Station	Velocity						Thickness						Depth		
	Sediment			Crust		Mantle	Water	Sediment			Crust		Crust	Moho	Ref.
	Uncon.	Semi.	Cons.	Cont.	Ocean.			Uncon.	Semi.	Cons.	Cont.	Ocean.			
Portland, Maine, Section—(contd.)															
2-W	1·62	—	—	5·85	—	—	0·26	0·15	—	—	—	—	0·41	—	5
37	1·79	—	—	6·04	—	—	0·26	0·07	—	—	—	—	0·33	—	5
36							0·23	0·07	—	—	—	—	0·30	—	
46	—	2·05	—	6·04	—	—	0·24	—	0·00	—	—	—	0·25	—	5
48							0·22	—	0·02	—	—	—	0·25	—	
49	—	2·02	—	5·79	—	—	0·22	—	0·03	—	—	—	0·25	—	5
47							0·21	—	0·15	—	—	—	0·36	—	
50	—	—	—	(5·52)	—	—	0·25	—	—	—	—	—	>0·25	—	5
44	1·83	—	—	5·48	—	—	0·23	0·19	—	—	—	—	0·42	—	5
45							0·21	0·05	—	—	—	—	0·27	—	
51	(1·81)	—	—	5·95	—	—	0·17	0·10	—	—	—	—	0·27	—	6
52							0·15	0·04	—	—	—	—	0·18	—	
53	(1·81)	—	—	5·12	—	—	0·13	0·07	—	—	—	—	0·20	—	6
54							0·07	0·20	—	—	—	—	0·27	—	
55	1·74	—	—	5·62	—	—	0·06	0·03	—	—	—	—	0·09	—	6
56							0·16	0·18	—	—	—	—	0·34	—	
57	(1·74)	2·28	—	5·05	—	—	0·08	0·11	0·87	—	—	—	1·06	—	6
58							0·08	0·21	0·68	—	—	—	0·98	—	
59	1·96	—	3·15	5·87	—	—	0·08	0·54	—	0·71	—	—	1·33	—	6
60							0·08	0·74	—	0·50	—	—	1·33	—	
61	(1·81)	—	(3·15)	(5·87)	—	—	0·08	0·91	—	1·31	—	—	2·30	—	6
62	1·71	2·52	3·51	5·84	—	—	0·06	0·45	0·94	2·04	—	—	3·49	—	6
63							0·06	0·49	1·24	1·26	—	—	3·05	—	

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64	1·74	2·17	3·49	5·60	—	—	0·06	0·36	1·33	1·36	—	—	3·11	—	6
65							0·07	0·19	0·87	1·52	—	—	2·66	—	
66	1·80	2·28	3·00	5·00	—	—	0·07	0·33	0·52	1·97	—	—	2·89	—	6
67							0·09	0·47	0·70	1·60	—	—	2·86	—	
68	1·67	2·78	3·96	5·08	—	—	0·09	0·64	1·19	1·21	—	—	3·15	—	6
69							0·16	0·68	1·21	1·40	—	—	3·25	—	
70	1·86	2·43	3·86	5·08 5·29	—	—	0·23	0·49	1·20	1·12	—	—	3·04 5·51	— —	6
71				5·02			2·23	0·66	0·52	3·24	—	—	4·62 6·65	— —	
72	—	2·50	3·63	4·69	6·66	—	1·92	—	2·88	1·72	4·93	—	6·52	—	6
73							2·74	—	2·99	2·13	5·07	—	7·86	—	
33E	(1·83)	(2·38)	(3·45)	5·23	—	—	0·18	0·54	0·95	1·56	—	—	3·23	—	6
33W							0·18	(0·77)	1·04	1·63	—	—	3·63	—	
32E	(1·82)	—	(3·94)	4·67	(6·47)	—	1·37	(1·38)	—	(2·17)	4·85	—	5·42	—	6
32W							2·01	1·38	—	1·89	(4·85)	—	5·28	—	
31E	(1·82)	(2·62)	3·92	5·02	6·88	—	2·31	1·30	1·59	2·24	(4·05)	—	7·44	—	6
31W							2·47	(1·30)	(0·95)	2·55	(2·84)	—	7·26	—	
30N	(1·65,	2·91	—	4·54	6·81	(8·06)	2·56	(1·65)	1·43	—	5·12	(9·95)	5·64	(20·71)	6
30S	1·83)						3·20	1·30	2·02	—	3·50	(4·04)	6·52	(14·06)	
Woods Hole Section															
1A	(1·71)	—	—	(5·72)	—	—	—	—	—	—	—	—	—	—	7
1A	1·71	—	2·97	5·70	—	—	0·02	0·21	—	—	—	—	0·23	—	7
3·2							0·05	0·21	—	0·46	—	—	0·72	—	
3·2	1·83	—	—	5·90	—	—	0·05	0·65	—	—	—	—	0·71	—	7
3A															
3A	1·80	—	—	5·59	—	—	0·07	0·72	—	—	—	—	0·78	—	7
4-3															
4-3	1·86	—	—	5·56	—	—	0·08	0·82	—	—	—	—	0·90	—	7
5															
5	1·83	—	—	5·72	—	—	0·12	1·44	—	—	—	—	1·56	—	7
6	(1·95)	—	—	(5·79)	—	—	—	—	—	—	—	—	—	—	7
76	1·63	2·13	4·06	5·83	—	—	0·13	0·29	1·00	0·83	—	—	2·33	—	6
77							0·22	0·38	0·94	1·27	—	—	2·82	—	

Table 1—continued

Station	Velocity						Thickness						Depth		
	Sediment			Crust		Mantle	Water	Sediment			Crust		Crust	Moho	Ref.
	Uncon.	Semi.	Cons.	Cont.	Ocean.			Uncon.	Semi.	Cons.	Cont.	Ocean.			
Woods Hole Section—(contd.)															
34	1·61	(2·84)	—	(5·08)	—	—	0·09	0·58	1·01	—	—	—	1·68	—	6
35							0·17	0·81	1·82	—	—	—	2·79	—	
78	1·68	2·01	3·90	5·26	—	—	0·22	0·24	0·97	1·78	—	—	3·21	—	6
79							0·53	0·46	0·89	0·87	—	—	2·74	—	
80				5·48			0·46	0·21	0·73	0·75	—	—	2·54	—	
				5·05									(2·90)	—	
	1·74	2·22	3·35	5·38	—	—							(7·46)	—	6
				5·09									(7·81)	—	
81							2·40	0·90	0·99	0·59	—	—	4·88	—	
74	1·87	2·26	—	4·51	7·43	—	2·69	0·63	1·64	—	4·71	—	4·95	—	6
82-75							2·72	1·00	2·00	—	6·98	—	5·72	—	
Scattered Profiles Gulf of Maine															
1W	1·62	—	—	5·06	—	—	0·10	0·09	—	—	—	—	0·20	—	5
1E							0·13	0·15	—	—	—	—	0·28	—	
2W	1·62	—	—	5·85	—	—	0·26	0·17	—	—	—	—	0·43	—	5
2E							0·23	0·14	—	—	—	—	0·37	—	
3W	—	—	3·72	6·07	—	—	0·18	—	—	0·49	—	—	0·68	—	5
3E							0·18	—	—	0·40	—	—	0·58	—	
4W	1·53	—	—	4·57,	—	—	0·21	0·01	—	—	0	—	0·21	—	5
4E				6·04			0·23	0·05	—	—	0·91	—	0·27	—	
5	1·53	—	—	4·57, 5·94	—	—	0·12 0·05	0·22 0	— —	— —	2·99 1·15	— —	0·34 0·05	— —	5

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ME (Falmouth)	—	—	—	5·3, (6·25)	—	—	0	—	—	—	5·1	—	0	—	8
South of Point Judith and Block Island														
MY	—	—	—	6·05	—	—	0	—	—	—	—	—	0	—	9
PR 43	1·79	—	—	5·68	—	—	0·03	0·29	—	—	—	—	0·32	—	10
PR 46							0·04	0·30	—	—	—	—	0·34	—	
PR 45	1·79	1·97	—	5·93	—	—	0·06	0·17	0·31	—	—	—	0·54	—	10
PR 44							0·06	0·19	0·35	—	—	—	0·59	—	
A179-19 N	1·74	—	—	6·05	—	—	0·06	0·52	—	—	—	—	0·58	—	9
A179-19 S							0·06	0·85	—	—	—	—	0·91	—	
18E	1·91	2·09	—	5·58	—	—	0·08	1·19	—	—	—	—	1·27	—	9
18W							0·08	0·61	0·37	—	—	—	1·06	—	
A196-1															11
Long Island Area															
19	(1·51)	—	—	5·83	—	—	0·01	0·04	—	—	—	—	0·05	—	10
									—	—	—	—	0·06		
									—	—	—	—	0·02		
20	1·74	—	—	5·38	—	—	0·01	0·04	—	—	—	—	0·06	—	10
22							0·01	0·11	—	—	—	—	0·12	—	
21							0·01	0·13	—	—	—	—	0·14	—	
23	1·60	—	—	5·30	—	—	0·01	0·12	—	—	—	—	0·13	—	10
24							0·01	0·08	—	—	—	—	0·09	—	
27	1·55	—	—	5·86	—	—	0·03	0·11	—	—	—	—	0·13	—	10
26A							0·02	0·13	—	—	—	—	0·15	—	
26	1·69	—	—	5·46	—	—	0·03	0·15	—	—	—	—	0·18	—	10
25							0·01	0·23	—	—	—	—	0·24	—	
32	(1·51)	—	—	5·25	—	—	0·01	0·04	—	—	—	—	0·05	—	10
33							0·03	0·02	—	—	—	—	0·05	—	
30	(1·51)	—	—	5·43	—	—	0·02	0·05	—	—	—	—	0·08	—	10
31							0·02	0·07	—	—	—	—	0·10	—	
29	1·68	—	—	5·49	—	—	0·02	0·21	—	—	—	—	0·23	—	10
28							0·01	0·20	—	—	—	—	0·21	—	
39	1·70	1·98	—	5·31	—	—	0·01	0·13	0·38	—	—	—	0·50	—	10
40							0·03	0·14	0·29	—	—	—	0·43	—	

Table 1—continued

Station	Velocity						Thickness						Depth		Ref.
	Sediment			Crust		Mantle	Water	Sediment			Crust		Crust	Moho	
	Uncon.	Semi.	Cons.	Cont.	Ocean.			Uncon.	Semi.	Cons.	Cont.	Ocean.			
Long Island Area—(contd.)															
42	1·79	2·00	—	5·91	—	—	0·05	0·18	0·46	—	—	—	0·69	—	10
41							0·05	0·19	0·59	—	—	—	0·83	—	
NE-SW AMB	1·73	2·08	—	5·58	—	—	0·02	0·24	0·30	—	—	—	0·57	—	12
NW-SE	1·70	2·09	—	5·73	—	—	0·02	0·24	0·32	—	—	—	0·58	—	
New York Section															
7	(1·71)	—	—	(5·73)	—	—	—	—	—	—	—	—	—	—	7
7	1·86	—	—	5·27	—	—	0·02	0·62	—	—	—	—	0·64		7
8	1·58	—	3·29	5·96	—	—	0·03	0·63	—	0·17	—	—	0·84	—	7
9							0·04	0·92	—	2·86	—	—	3·62	—	
9	1·75	—	3·44	5·53	—	—	0·05	0·95	—	3·88	—	—	4·88	—	7
9′	1·75	—	3·44	5·65	—	—	0·07	0·92	—	2·83	—	—	3·83	—	7
10	1·75	—	3·32	5·38	—	—	0·06	1·06	—	3·35	—	—	4·47	—	7
11	1·78	—	3·63	5·46	—	—	0·12	1·19	—	2·20	—	—	3·52	—	7
12	(1·68)	—	(3·63)	(5·46)	—	—	—	—	—	—	—	—	—	—	7
86	1·83	—	3·74	5·35	—	—	0·14	1·10	—		—	—	2·81	—	6
									—		—	—	2·16	—	
85							1·53	0·89	—	2·25	—	—	4·67	—	

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84				5·36	—	—	1·62	0·87	—	2·07	—	—	4·56	—	
				(4·80)	—	—			—		—	—	6·63	—	
	1·76	—	3·74	(4·80)	—	—			—		—	—	6·16	—	6
				5·18	—	—			—		—	—	7·04	—	
83							2·72	2·78	—	1·63	—	—	7·13	—	
Barnegat Section															
1	(1·22)	—	—	(5·73)	—	—	—	0·05	—	—	—	—	0·02	—	13
2	1·62	2·18	—	5·64	—	—	—	0·07	0·13	—	—	—	0·17	—	13
3	(1·67)	1·95	—	5·52	—	—	—	0·11	0·08	—	—	—	0·15	—	13
4	0·48, 1·71	2·12	—	6·42	—	—	—	0·25	0·11	—	—	—	0·31	—	13
5	(1·57)	(1·83)	—	(4·88)	—	—	—	0·03	0·33	—	—	—	0·32	—	13
6	0·48, 1·70	2·41	—	3·96	—	—	—	0·32	0·14	—	—	—	0·42	—	13
7	(1·65)	(1·89)	—	(4·33)	—	—	—	0·08	0·43	—	—	—	0·49	—	13
8	(1·63)	(1·94)	—	(5·73)	—	—	—	0·09	0·58	—	—	—	0·67	—	13
Cape May Section															
1	0·91, 1·36	—	—	5·23	—	—	—	0·06	—	—	—	—	0·06	—	14
2	0·91, 1·68	—	—	5·36	—	—	—	0·09	—	—	—	—	0·09	—	14
3	(0·91, 1·79)	—	—	(5·25)	—	—	—	0·16	—	—	—	—	0·16	—	14
4	0·91	1·92	—	5·97	—	—	—	0·02	0·38	—	—	—	0·40	—	14
5	0·91, 1·55	2·05	—	5·35	—	—	—	0·11	0·40	—	—	—	0·51	—	14
6	0·91, 1·63	2·12	—	5·39	—	—	—	0·14	0·52	—	—	—	0·66	—	14
7	0·91, 1·60	1·78, 2·36	—	5·50	—	—	—	0·10	0·64	—	—	—	0·74	—	14
8	0·91, 1·67	2·42	—	5·51	—	—	—	0·39	0·66	—	—	—	1·05	—	14
9	(0·91, 1·63)	(2·33)	—	(6·07)	—	—	—	0·38	0·78	—	—	—	1·16	—	14

Table 1—continued

Station	Velocity						Thickness						Depth		Ref.
	Sediment			Crust		Mantle	Water	Sediment			Crust		Crust	Moho	
	Uncon.	Semi.	Cons.	Cont.	Ocean.			Uncon.	Semi.	Cons.	Cont.	Ocean.			
Cape May Section—(contd.)															
10	(0·91, 1·66)	(2·63)	—	(5·07)	—	—	—	0·55	0·85	—	—	—	1·40	—	14
11	(0·91, 1·70)	(2·00)	—	—	—	—	—	0·69	—	—	—	—	—	—	14
12	(0·91, 1·67)	(2·16)	—	—	—	—	—	0·30	—	—	—	—	—	—	14
13	(1·68)	—	(2·99)	(5·94)	—	—	—	—	—	—	—	—	—	—	7
13	1·66	—	3·08	5·47	—	—	0·01	0·71	—	2·96	—	—	3·68	—	7
13′							0·03	0·91	—	2·85	—	—	3·78	—	
13′ 14	1·66	—	3·31	5·53	—	—	0·04	0·86	—	3·41	—	—	4·31	—	7
14 14′	1·60	—	3·35	5·44	—	—	0·04	0·84	—	3·73	—	—	4·61	—	7
14′ 15	1·60	—	3·64	5·46	—	—	0·05	1·20	—	4·05	—	—	5·17	—	7
15 15′	1·68	—	3·93	5·62	—	—	0·06	1·23	—	3·97	—	—	5·25	—	7
15′ 16	1·68	—	4·18	5·72	—	—	0·12	1·45	—	2·72	—	—	4·28	—	7
16	(1·63)	—	4·33	—	—	—	—	—	—	—	—	—	—	—	7
G-16N	1·68	2·54	4·12	5·46	7·13	—	2·08	0·74	1·93	3·61	4·57	—	8·46	—	4
G-16S							2·49	0·51	1·59	3·32	5·08	—	7·91	—	

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Cape Henry Section														
1	(1·94)	—	—	(3·75)	—	—	—	0·10	—	—	—	—	0·10	—	15
2	(1·69)	—	—	(3·92)	—	—	—	0·12	—	—	—	—	0·12	—	15
3	(0·61, 1·83)	—	—	(6·35)	—	—	—	0·13	—	—	—	—	0·13	—	15
4	(0·61, 1·75	—	—	(5·59)	—	—	—	0·12	—	—	—	—	0·12	—	15
5	(0·61, 1·57)	—	—	(5·22)	—	—	—	0·11	—	—	—	—	0·11	—	15
6	(0·61. 1.49)	—	—	(4·63)	—	—	—	0·28	—	—	—	—	0·28	—	15
7	1·72	—	—	5·73	—	—	—	0·35	—	—	—	—	0·35	—	15
8	(1·64)	(1·93)	—	5·92	—	—	—	0·17	0·23	—	—	—	0·40	—	15
9	(1·72)	(2·05)	—	6·15	—	—	—	0·18	0·41	—	—	—	0·59	—	15
10	(1·61)	(2·07)	—	5·79	—	—	—	0·32	0·37	—	—	—	0·69	—	15
11	(0·61, 1·69)	—	—	(5·32)	—	—	—	0·48	0·40	—	—	—	0·88	—	15
12	(1·72)	(2·33)	—	(5·24)	—	—		0·54	0·74	—	—	—	1·28	—	15
13	(1·72)	(2·27)	—	(5·77)	—	—		0·33	1·65	—	—	—	1·98	—	15
14	(1·71)	(2·49)	—	(5·49)	—	—		0·24	> 3·23	—	—	—	> 3·47	—	15
15	(1·72)	(2·56)	—	(5·49)	—	—		0·14	> 3·60	—	—	—	> 3·74	—	15
North Carolina Coastal Plain														
1NW	(0·91,						—	0·12	—	—	—	—	0·12	—	
1SE	1·76)	—	—	5·58	—	—	—	0·10	—	—	—	—	0·10	—	16
2W							—	0·01	0·32	—	—	—	0·33	—	
2E	(0·91)	2·01	—	5·78	—	—	—	0·01	0·32	—	—	—	0·33	—	16
3W							—	0·02	0·70	—	—	—	0·72	—	
3E	(0·91)	2·07	—	6·08	—	—	—	0·02	0·88	—	—	—	0·90	—	16
4S							—	0·02	0·65	—	—	—	0·67	—	
4N	(0·91)	2·29	—	5·76	—	—	—	0·02	0·64	—	—	—	0·66	—	16
5SW							—	0·02	0·54	—	—	—	0·56	—	
5NE	0·81	2·12	—	6·08	—	—	—	0·02	0·56	—	—	—	0·58	—	16
6SW							—	0·04	0·56	—	—	—	0·60	—	
6NE	(1·53)	2·01	—	5·84	—	—	—	0·05	0·62	—	—	—	0·67	—	16
7SW	(1·53),						—	0·21	0·78	—	—	—	0·99	—	
7NE	1·70	2·17	—	5·79	—	—	—	0·11	0·90	—	—	—	1·01	—	16

Table 1—continued

Station	Velocity						Thickness						Depth		Ref.
	Sediment			Crust		Mantle	Water	Sediment			Crust		Crust	Moho	
	Uncon.	Semi.	Cons.	Cont.	Ocean.			Uncon.	Semi.	Cons.	Cont.	Ocean.			
North Carolina Coastal Plain—(contd.)															
8S	(0·98),	2·53	—	6·07	—	—	—	0·16	1·21	—	—	—	1·37	—	16
8N	1·78						—	0·17	1·20	—	—	—	1·37	—	
9NW	0·97,	2·81	—	5·34	—	—	—	0·49	1·04	—	—	—	1·53	—	16
9SE	1·78						—	0·49	1·26	—	—	—	1·75	—	
10S	0·98,	2·87	—	5·91	—	—	—	0·14	1·73	—	—	—	1·87	—	16
10N	1·89						—	0·19	1·54	—	—	—	1·73	—	
12SW	1·49,	2·45	3·41	5·76	—	—	—	0·07	1·04	1·51	—	—	2·62	—	16
12NE	1·83						—	0·12	(1·04)	1·48	—	—	2·64	—	
14S	1·53	2·07,	3·37	5·81	—	—	—	0·06	1·50	1·27	—	—	2·83	—	16
14N		2·82					—	0·06	1·21	1·20	—	—	2·47	—	
17N	1·53	1·88	3·24	5·76	—	—	—	0·07	1·05	0·54	—	—	1·66	—	16
17S							—	0·06	0·91	0·90	—	—	1·87	—	
18NW	(1·53)	(1·88)	(3·24)	6·00	—	—	—	0·07	0·98	0·52	—	—	1·57	—	16
18SE							—	(0·07)	1·05	0·47	—	—	1·59	—	
Scattered Profiles															
A196-2			3·60		—	—								—	11
15				5·32	—	—							3·55	—	11
14				6·14	—	—							3·20	—	11
13			3·87		—	—								—	11
3				5·48	—	—							1·14	—	11
12				5·90	—	—							1·42	—	11
11				5·93	—	—							1·83	—	11
Mathews	(1·55)	(2·22)	—	6·01	—	—	—	0·34	0·31	—	—	—	0·65	—	15
M27-Shoal	(1·80)	—	—	4·62	—	—	0·01	0·94	—	—	—	—	0·94	—	17
M27-Deep	(1·85)	(2·13)	—	5·52	—	—	0·03	0·33	0·58	—	—	—	0·91	—	17

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reversed velocities over each portion should differ; if the break is due to a change in slope, these true velocities should be the same. Should these phenomena occur simultaneously, a solution might be difficult or even impossible to work out without supplementary data.

The possibility of low velocity layers under higher velocity layers is always present. These will not be detected by the standard seismic refraction method, but indications of their presence may be seen under some conditions if the geometry of the system is favourable.

Finally, one is sometimes faced with the choice of drawing a smooth curve or a number of straight line segments through a series of points. This is particularly true of the arrivals from the sedimentary layers. The depths obtained by dividing the curve into straight line segments will not be appreciably different from those obtained using the curve, but as EWING and LEET (1932, p. 6) point out, ". . . it is a serious error to attribute significance to the arbitrary set of lines used".

The terminology used for the different layers is approximately that of the papers of the Geophysical Investigations series.

1. *Sedimentary layers*—includes layers with velocities from 0·4 to about 4·2 km/sec. For plotting purposes these have been divided into three groups: unconsolidated, semi-consolidated, and consolidated sediments. The seismic discontinuities as shown do not necessarily represent stratigraphic horizons.

2. *Continental crust or basement*—includes velocities from about 4·0 km/sec to about 6·3 km/sec. The discontinuity is traced from place to place on the basis of its position. It may represent a great variety of materials from metamorphic and igneous rocks to volcanics and sediments. No age connotation is indicated. This layer does not appear to be present under the oceans.

3. *Oceanic crust*—the layer with velocities varying from 6·4 to 7·6 km/sec which constitutes the uppermost high velocity layer in the ocean basins. There is serious doubt whether this layer continues as a discrete unit under the continents.

4. *Mantle*—velocities in the upper part of this layer vary from 7·8 to about 8·3 km/sec. The top of this layer is about 10 km beneath the surface of the oceans and equivalent velocities are found on the order of 35 km under the continents. The discontinuity at the top of this layer is called the Mohorovicic discontinuity under the latter and it is generally accepted that the discontinuity at 10 km under the oceans represents the same change in rock character.

Although this is usually supposed to be the uppermost discontinuity which is world-wide in scope, there is reason to believe that it is not a sharp break in certain special areas. It is quite possible that in active volcanic or orogenic belts the discontinuity is displaced and temporarily obscured by the igneous activity.

DISCUSSION OF NEW TRAVEL TIME DATA

The results of the travel time data are presented in Table 1 as shown on pp. 114–126. Since the best method of presentation of these data is in the form of sections, the new stations have been placed indiscriminately among the old, as noted in the references.

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As many of the new stations are straightforward and simple, only those which presented problems in interpretation or have possible ambiguous results are discussed and have their travel time curves presented. These problem profiles are the ones which cover the area between the approximate limits of the 100 fathom curve and the 1000 fathom curve. They present difficulties due to both ocean bottom and sub-bottom topography and due to the difficulty mentioned earlier when the upper layers are observed over only a part of the profile as first arrivals. Enough data are available on both the forward and reverse ends so that these difficulties can, in most cases, be resolved.

Profiles LRB 68-69, 70-71, 72-73

These three reversed profiles form a line extending from 50 fathoms to 1500 fathoms off the south-west end of Georges Bank. Profiles 68-69 and 72-73 are both straightforward and are included to show how they fit the ends of Profile 70-71 which is between them.* Profile 68-69 (Fig. 2) shows four layers, three

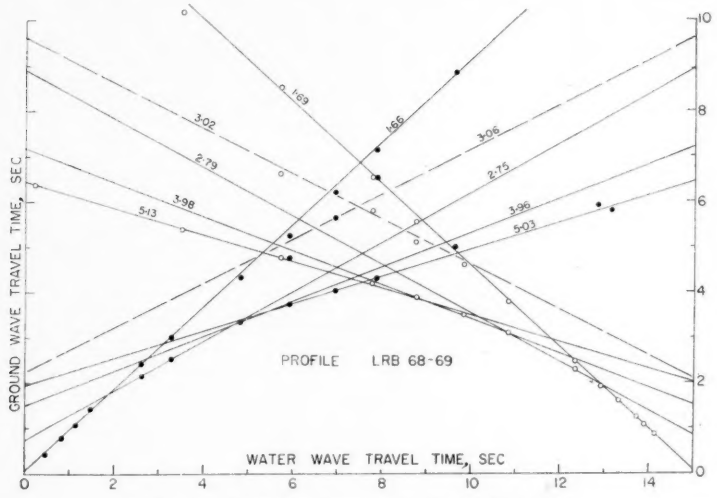

Fig. 2. Travel time curves, Profile LRB 68-69.

of which are well determined with some scattering of the points. The fourth layer is represented by three points on the south end but is poorly determined on the north.† All of the lines reverse well. Profile 72-73 (Fig. 3) did not show the lowest velocity layer of 68-69, and, since the uppermost observed layer was represented by a line tangent to the reflection curve, this layer, if present, must be thin. A deeper layer was observed on this profile which was not represented on 68-69.

* The numbers corresponding to each line segment on the travel time graphs are the apparent velocities in km/sec. When bottom reflection curves are plotted they are designated R.

† The dashed lines do not represent an additional layer but are interpreted as shear wave arrivals. In order for the intercepts to give depths comparable to those from the compressional wave arrivals, it must be assumed that conversion to shear waves took place at the top of or within the sedimentary column (NAFE and DRAKE, 1957).

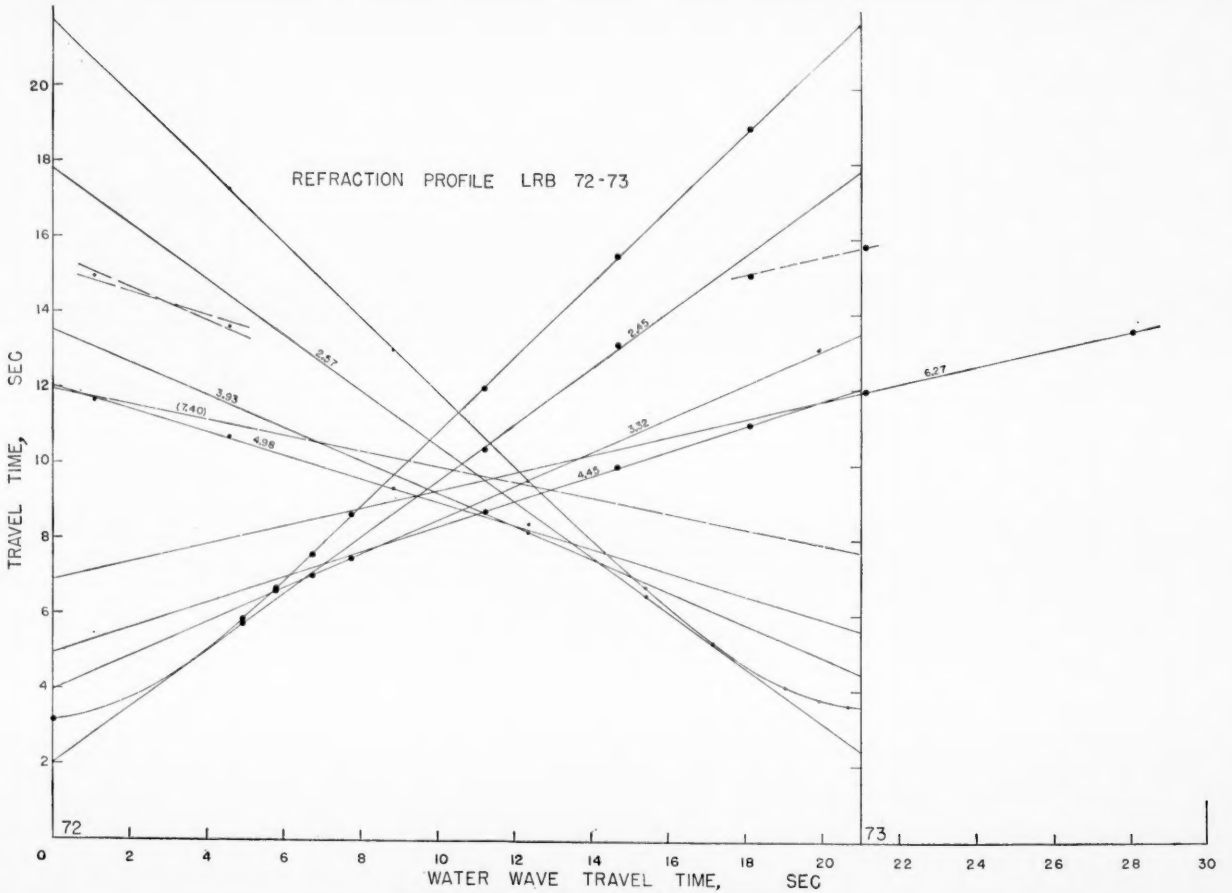

Fig. 3. Travel time curves, Profile LRB 72-73.

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Profile 70-71 (Fig. 4), between these two, is not so simple. Here the interpretation is based on a division of the profile into three parts and insertion of fictitious stations (see EWING *et al.*, 1950, e.g., p. 880). It was assumed that the topography represented by the breaks in the high velocity line was confined to the upper interface of this layer and that the layers above this were planar. The depth to the high velocity layer on station 70 was taken to be the same as for station 69 and that for station 71 the same as for 72. Using these assumptions

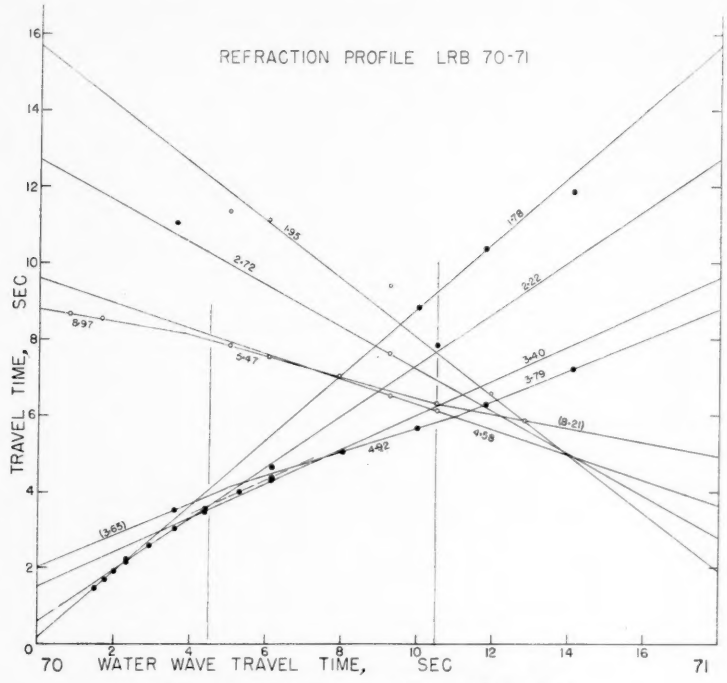

Fig. 4. Travel time curves, Profile LRB 70-71.

it was possible to calculate the slopes of the three sections and estimate the depths at the two fictitious points. The interpretation is in good agreement with the results of the A164 stations to the west.

Profiles LRB 78-79, 80-81, 74-75

This group of profiles form an extension of the Woods Hole section from the 100 to the 1500 fathom curve and the results are quite similar to those of the previous group. Four layers are indicated on Profile 78-79 (Fig. 5) as was the case for the shallow profile (68-69) above. Additional arrivals giving two reversed lines which do not represent an additional layer have been interpreted as shear waves as in this profile.

Once again the uppermost layer appears to be thin or absent on the deep profile (74-75, Fig. 6). It may be noted that the uppermost layer determined on this profile has a velocity intermediate between the velocities of the two upper

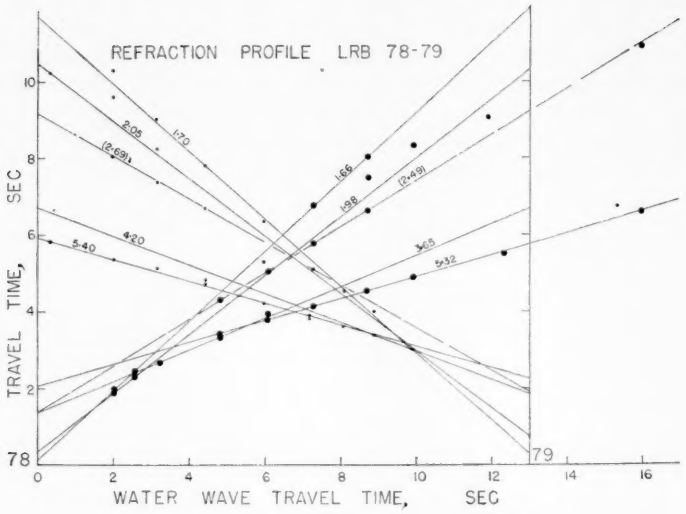

Fig. 5. Travel time curves, Profile LRB 78-79.

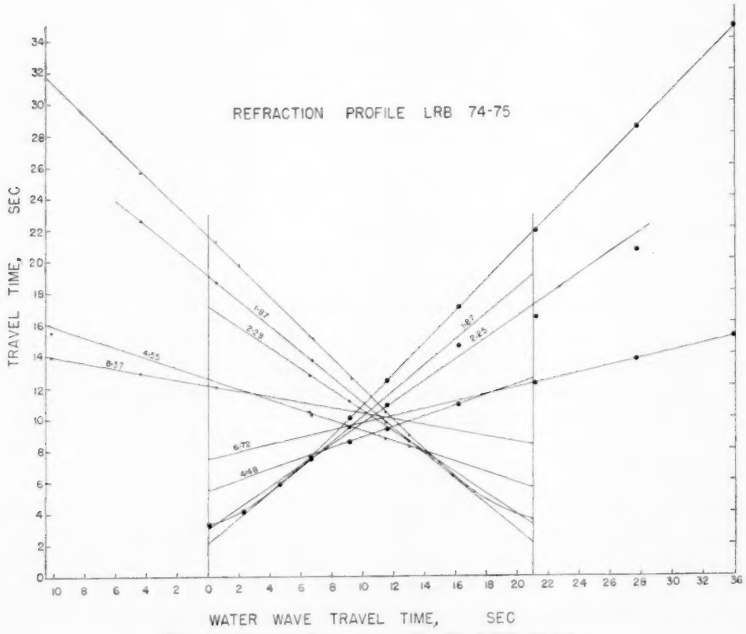

Fig. 6. Travel time curves, Profile LRB 74-75.

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layers of 78-79. It has been shown by model studies (PRESS *et al.*, 1954, p. 400) that such velocities may result if layer thicknesses are of the same order as the wavelengths of the sound arrivals. A deeper layer was found on Profile 74-75 which was not observed on the shallow profile. This layer is well determined on both ends of the profile.

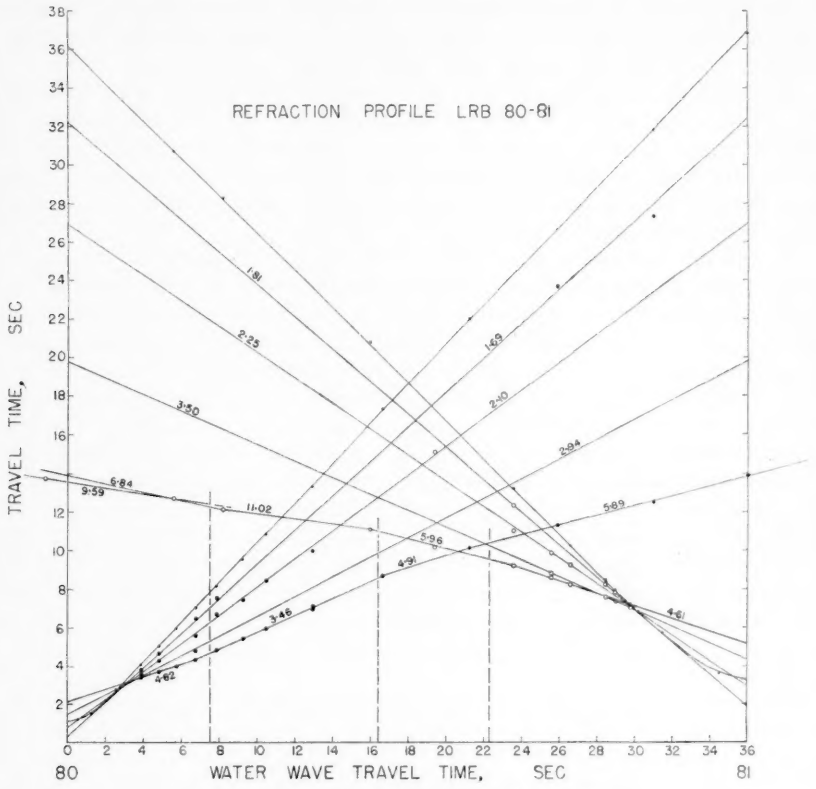

Fig. 7. Travel time curves, Profile LRB 80-81.

Profile 80-81 (Fig. 7) is even more complicated than its counterpart on the previous section. In this case it was necessary to divide the profile into four parts. The upper three layers were carried as planes along the full length of the profile. The underlying layer was divided by three fictitious stations into four parts. There were sufficient points along these lines that each of these segments could be reversed and "true" velocities and slopes determined. The resultant velocities are not in all cases the same although of the same order. Some errors in the depths may be expected to result since the calculations assume a constant velocity within any one layer.

The most distant point of station 81 shows evidence of the deeper layer found on Profile 74-75. There are not enough data to draw any conclusions other than that the layer is dipping toward the ocean at this point.

Profiles A172 30-33

Between the seaward extensions of the Woods Hole and Portland sections four reversed profiles were observed. Profile 30 (Fig. 1), on the continental rise, is oriented perpendicular to the edge of the shelf with the water depth varying between 1400 and 1750 fathoms. The other three profiles are nearly parallel to the topographic contours. Profile 31, also on the continental rise, is in 1300 fathoms of water; Profile 32, at the base of the slope, 1050 fathoms; and Profile 33, near the edge of the shelf, 100 fathoms.

No structural complications are exhibited under Profile 30 (Fig. 8). Beneath the many upper layers, determined by second arrivals, the continental and oceanic crustal layers are well determined and a single early arrival suggests penetration to the mantle. If a mantle velocity of 8·1 km/sec is assumed, minimum depths to the mantle of 14 and 21 km under the seaward and shoreward ends of the profile may be determined.

An offset of the highest velocity line in one place and a change in its slope in another indicate considerable structure under Profile 31 (Fig. 9). This profile has been interpreted using the buried topography corrections of SUTTON and BENTLEY (1953). This method differs from that used previously in that, instead of carrying the structure through the profile by following the variations of the data, a mean base line is constructed as an average over the length of the profile and then structure is introduced to account for the deviations from this line. The net result using either of the methods is the same. The results from Profile 31 show the eastern end to be lowered by 3·4 km as indicated by the offset in the travel time curve and a trough-like feature on the western end as indicated by the change in slope of the curve. Since the profile is slightly oblique to the overall structure and the effects of drift of the recording vessel may be quite important in regions of complicated structure, it is not possible to determine the exact relationship between the internal structure of this profile and the overall structure of the area. In general there is good agreement with the adjacent sections.

No data were observed on the uppermost layer of Profile 32 (Fig. 10) although its presence is indicated by the fact that the travel time line of the first observed layer cuts the reflection curve rather than being tangent to it. A velocity of 1·82 km/sec was assumed for the uppermost layer and was used in the calculations. No internal structure was observed on this profile, possibly because the data are too meagre to reveal it.

A horst-like feature is indicated by an offset in the high velocity line of Profile 33 (Fig. 11). The elevation change amounts to about 0·9 km. A feature similar to this is found on other sections along the coast near the edge of the shelf. Here again it was necessary to assume an upper layer, in this case to make the computed water depth agree with that determined by the echo sounder.

Profiles LRB 83-84, 85-86

These profiles caused the most difficulty for two reasons: the location and length of the profiles made bottom topography a more important problem, and the apparent velocities were such as to make it difficult to decide whether a segment represented a deeper layer or merely a change in slope.

It was necessary to divide Profile 85-86 (Fig. 12) into two parts on the basis

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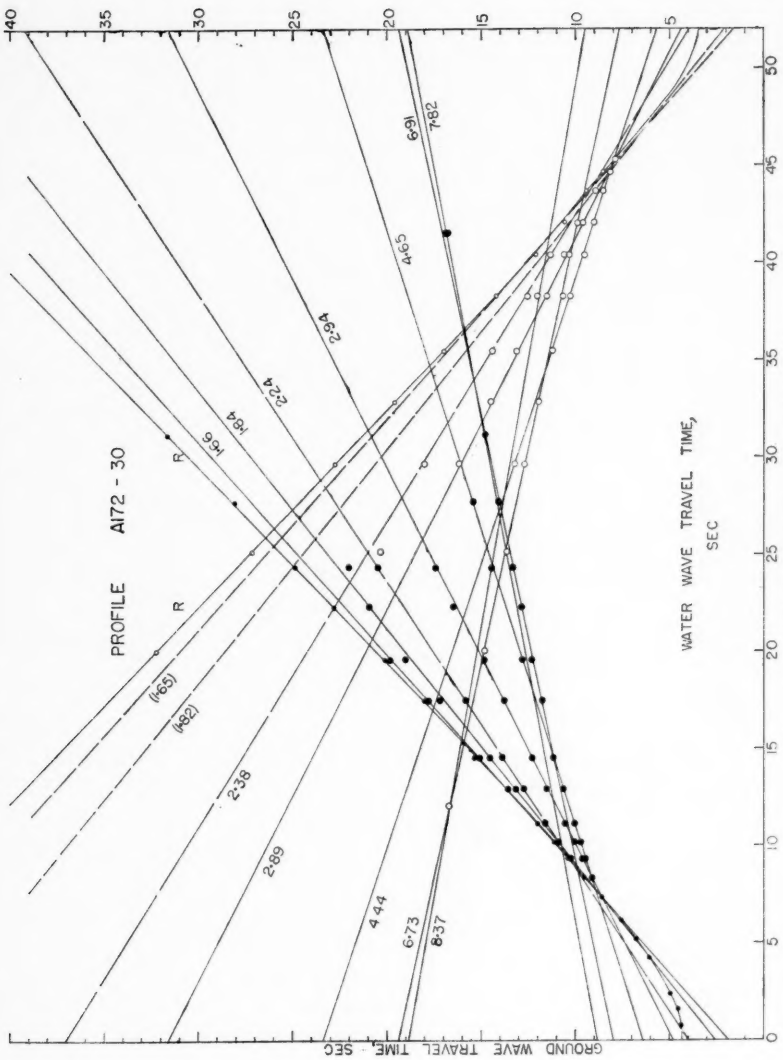

Fig. 8. Travel time curves, Profile A172-30.

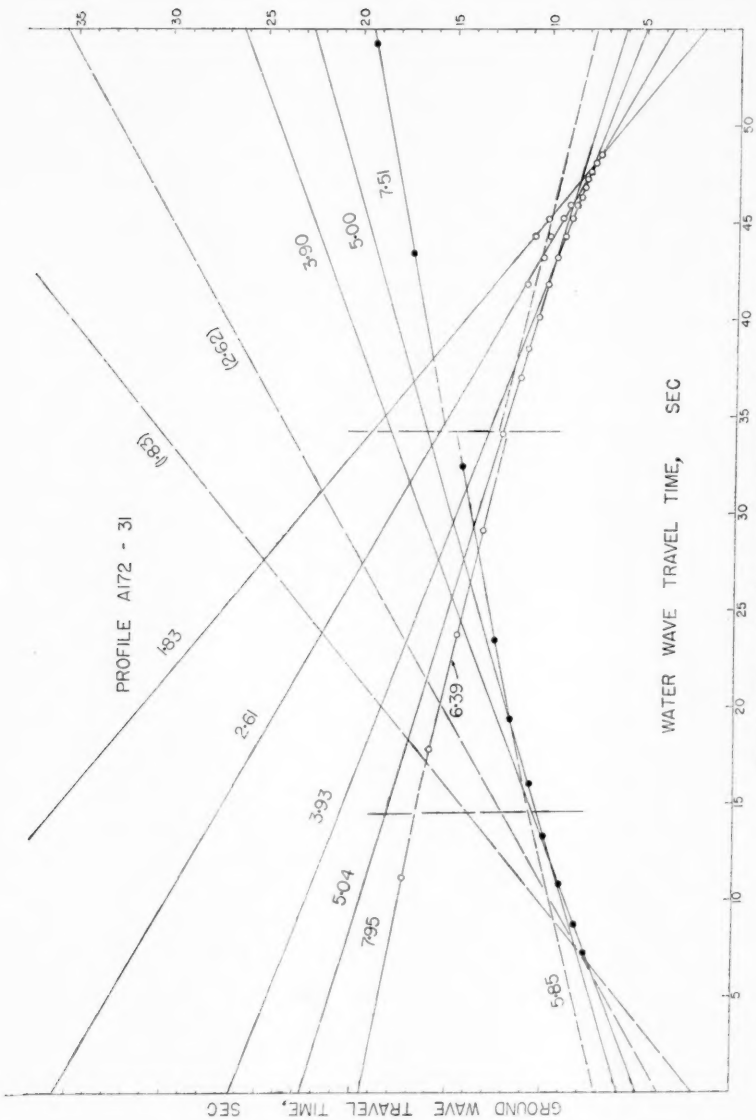

Fig. 9. Travel time curves, Profile A172-31.

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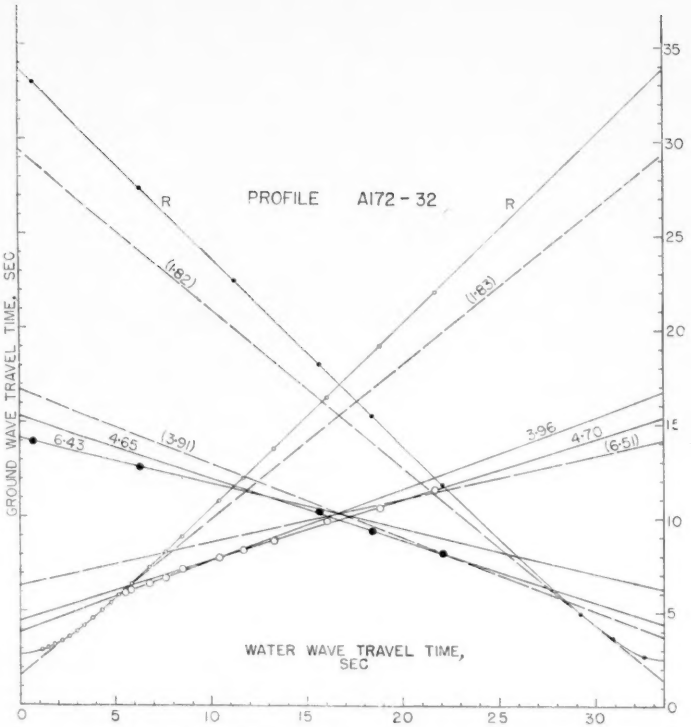

Fig. 10. Travel time curves, Profile A172-32.

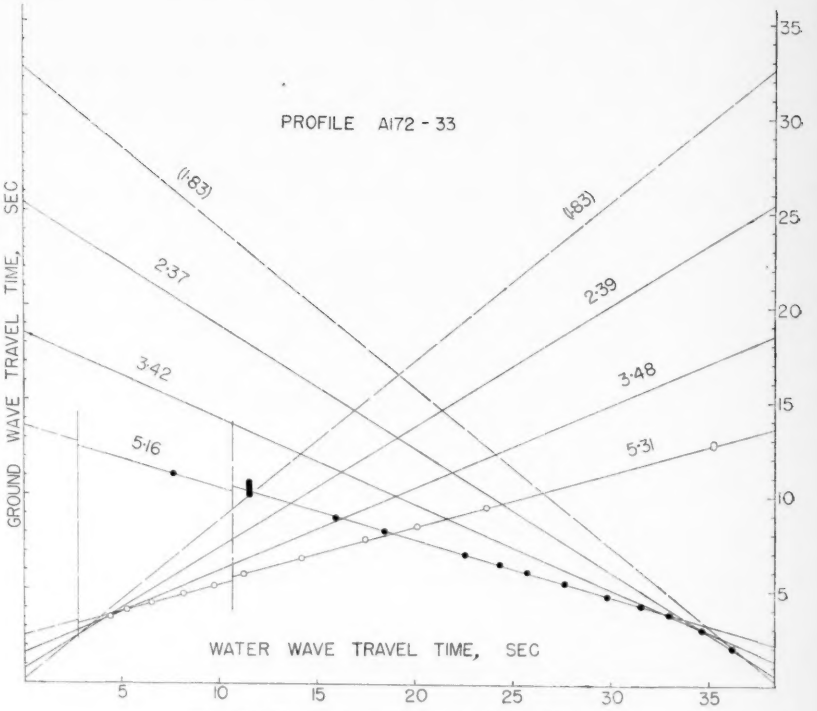

Fig. 11. Travel time curves, Profile A172-33.

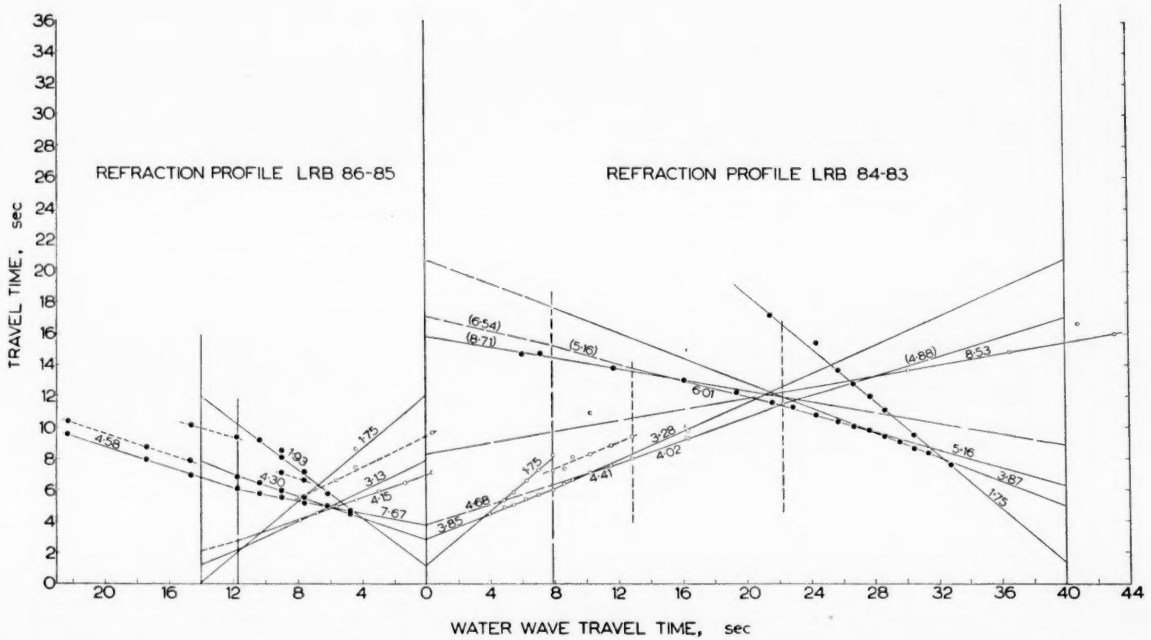

Fig. 12. Travel time curves, Profiles LRB 86-85, 84-83.

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of bottom topography. The part closest to station 86 was on the shelf while the remainder of the profile was on the slope. The slope part is well determined but only the basement layer was observed on the shelf and only on one end of the profile. In order to find the slope of this layer, it was necessary to use the true velocity found from the slope part of the profile. Depths could be determined at the fictitious station, but due to uncertainty of behaviour of the upper layers, only an approximate dip of the basement layer was calculated on the shelf part and found to be consistent with the results of the adjacent profile (V, No. 12, Fig. 1).

Profile 83-84 (Fig. 12) was divided into two parts on the basis of bottom topography and the deep end further divided into three parts due to changes in the configuration of the basement layer. Some uncertainty arose from the lack of knowledge about the exact configuration of the upper layers. These layers were assumed to be planar in each of the divisions determined by bottom topography.

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On only one of the sections of this profile was the basement velocity determined on both ends. The resultant true velocity was used to calculate the slopes of the other parts.

The deepest layer observed here had very high apparent velocities on both ends. If these lines are reversed in the normal manner, one finds a resultant "true" velocity of about 8·5 km/sec. It may be noted that the arrivals on these high velocity lines are at the limits of the profile and that they do not overlap. If there is a change in slope so that this layer dips up toward the ends of the profile and down toward the middle, the apparent velocities on both ends would be high. Since there are indications that this sort of structure exists on some of the other sections, such an interpretation has been accepted here. The resultant velocity would then more closely approach those measured elsewhere.

DISCUSSION OF VELOCITIES

To construct a geologic cross-section from seismic measurements, it is necessary to relate the observed velocities with rock type. Several factors must always be considered in order to determine the values of compressional wave velocity which best represent each unit.

PRESS *et al.* (1954, p. 388–401) have shown that unless a buried layer has a thickness of at least several wavelengths the observed velocity will differ from the body wave velocity characteristic of the material of the layer. Since the period increases with distance travelled (GUTENBERG, 1929; HARRIS and HASKELL, 1940, p. 194; BERZON, 1956, pp. 3–22) and since velocities normally increase with depth, the thickness necessary to give a true velocity must be greater at depth than near the surface. Thus for a surface layer of a given thickness the observed velocity might equal the true velocity whereas the two velocities might differ considerably for a layer of the same thickness at depth.

It must be remembered that velocity determined for a specific layer is the mean velocity over the line over which the measurements are made. Thus on the longer profiles more averaging is done and less detail of the velocity variation may be seen. Furthermore, since only a portion of a seismic profile shows first arrivals from any particular layer, it is possible that the forward and reverse end observations on segments of a profile are through different parts of a layer

and that there is a real difference in the velocity or the attitude of the layer at these two places. If structure is present in the upper layers of a profile, this structure will decrease the accuracy of the measurements in the underlying layers. Insufficient data may permit several interpretations of the structure with some resulting differences in calculated velocities.

Many sedimentary and metamorphic materials are not isotropic and compressional wave velocities measured with different orientations with respect to bedding or structure may differ by as much as 20 per cent. These differences should be minimized if the rocks are water saturated and deeply buried.

If a velocity gradient, such as may be present in the sediments, exists, the number of straight lines chosen to approximate the data and the slopes of these lines will be a function of the data density and location. Similarly, if two layers with little difference in velocity are superimposed, they may be interpreted as one if the data are insufficient.

In the light of these possible sources of error velocities are surprisingly consistent. In spite of the fact that the measurements used in this paper were made over a period of more than twenty years, using a variety of methods and with varying degrees of accuracy, it was not necessary to discard any of the data or to alter any of the previous results in order to make a consistent picture.

SEDIMENTARY VELOCITIES

The velocity of elastic waves in the sedimentary rocks of the area covered by this paper has been studied in detail by NAFE and DRAKE (1957). It was found

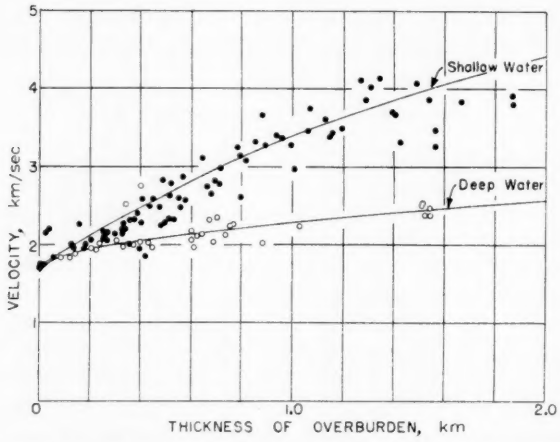

Fig. 13. Variation of compressional wave velocity with depth in the sediments.

that, in the gross, the velocity in the shallow water sediments (< 100 fathoms) varied with depth in a systematic manner approximated by the expression $V=1{\cdot}70 + 4{\cdot}30\{1-\exp(-Z/2)\}$ where V is the velocity in kilometres per second at a depth of burial of Z km. This expression gives a velocity at the surface of the sediment of 1·70 km/sec and approaches an upper limit of 6 km/sec. The gradient in the upper 2 km of deep water oceanic sediments (> 1500 fathoms) is

somewhat lower and may be expressed by $V = 1{\cdot}65 + 0{\cdot}64\sqrt{Z}$. The velocities at intermediate depths (100–1500 fathoms) fell between these two extremes (Fig. 13). An expression was derived relating the compressional wave velocity to certain physical properties of the sediments. It was found that the porosity, density, shear velocity, and elastic constants could be predicted with good accuracy from compressional wave velocity.

The compressional wave velocity within the sediments is closely related to the porosity (NAFE and DRAKE, 1957), and since the observed velocity–porosity relationship is independent of depth of water or depth of burial, the porosity of sediments at a given depth of burial in shallow water must be less than that for a corresponding depth in deep water. Hence the degree of cementation or lithification must be greater at a given depth on the shelf than in the ocean basin.

It has been suggested (NAFE and DRAKE, 1957) that circulation of water within the shallow-water sediments and the purely salt-water environment of the deep-water sediments are major factors contributing to the velocity differences found in these two environments. The deposition of material carried by circulating waters and the cementation possible under these conditions must have a strong effect on the velocities. The shallow-water sediments will also be influenced greatly by changes in water level. If the sediments are exposed and erosion removes a portion of them, it would be unlikely that the velocities in the remaining sediments would be reduced by the same amount that they were increased due to compaction and cementation. This process would tend to produce higher velocities at shallower depths.

The velocity gradient for the sediments off the coast of eastern North America north of Cape Hatteras is in good agreement with those from continental shelf environments off the south coast of Spain (DRAKE *et al.*, 1958) and in the Gulf of Mexico (EWING *et al.*, 1955), but somewhat higher than the gradients on land in the Gulf Coast or Mid-Continent areas. Measurements by HERSEY *et al.* (1958) in the Blake Plateau area (Fig. 14) indicate that the same limit of 6 km/sec is approached, but at a more rapid rate. This result might be attributed to cementation since this area contains a high proportion of carbonate rocks.

The shallow water results allow us to draw several conclusions about the sediments. First of all, since the measurements are scattered about a single curve, the suggestion arises that the sediments taken as a whole may be considered as a single unit without major breaks in either time or degree of lithification. Seismic velocities in areas where discontinuities are known to be present, such as in the Triassic fault basins (see, e.g. DRAKE *et al.*, 1954) do not fit the general curve.

Secondly, it is apparent that stratigraphic correlations of these sediments on the basis of velocity are not justified in this area since the velocity is mainly a function of depth of burial. Furthermore, the seismic layering may represent a choice of straight lines to best fit points on a curve rather than geologic horizons. This is borne out by a comparison of the seismic results with well logs.

EWING *et al.* (1940) correlated the two seismic discontinuities found within the sediments and the Manasquan–Vincetown and Magothy–Raritan contacts. The former appeared to be rather well determined; the latter was compared with only one well since others did not identify the contact. The Cape May line showed similar discontinuities which were correlated with the above on the basis of similarity of observed velocities, dip, and rate of thickening.

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SUTER *et al.* (1949) placed the Magothy–Raritan contact at — 859 ft in the deep well at Long Beach, Long Island (Fig. 34, No. 12). While this contact did not appear on station 7 of the New York Line (Fig. 1), a discontinuity was found at — 860 in a refraction station (Fig. 1, AMB) reported by CARLSON and BROWN (1955, p. 974). A comparison of Suter's contour map of the Magothy–Raritan contact (SUTER, 1949, Plate XVI) with the results of station 39 off

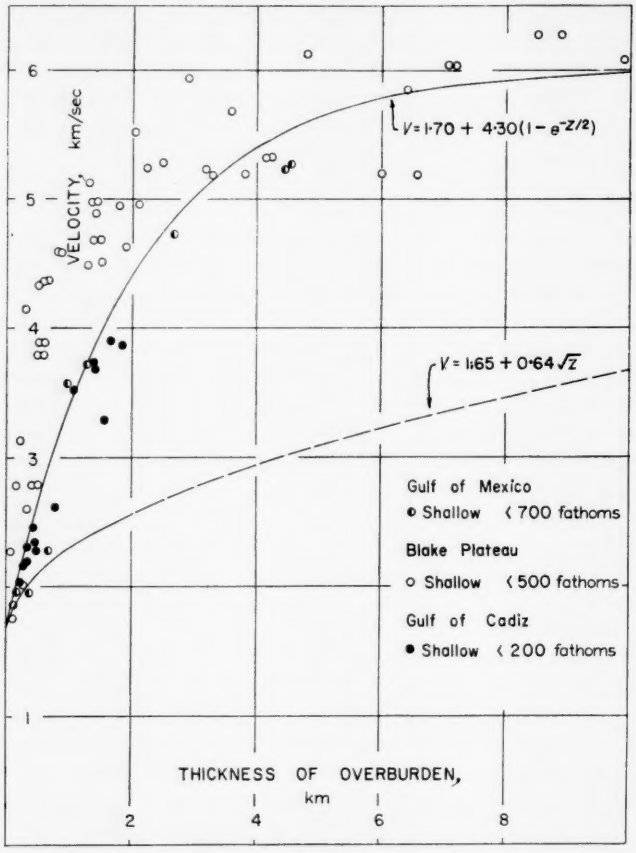

Fig. 14. Velocity–depth variations in sediments of the Blake Plateau, the Gulf of Mexico, and the Gulf of Cadiz.

Shinnecock Inlet, Long Island (OLIVER and DRAKE, 1951), fails to show agreement. The contact is at about — 1350 ft while the seismic discontinuity appears at — 443 ft. The Standard Oil Co. of New Jersey's North Carolina refraction results likewise fail to define specific stratigraphic horizons. There is some correlation between the depths of the Pliocene–Miocene contact and the first interface of the refraction work, but the lower discontinuities fall variously in the middle of the Tuscaloosa, between Tuscaloosa and Washita-Fredericksburg, between Black Creek and Magothy, and within the Miocene.

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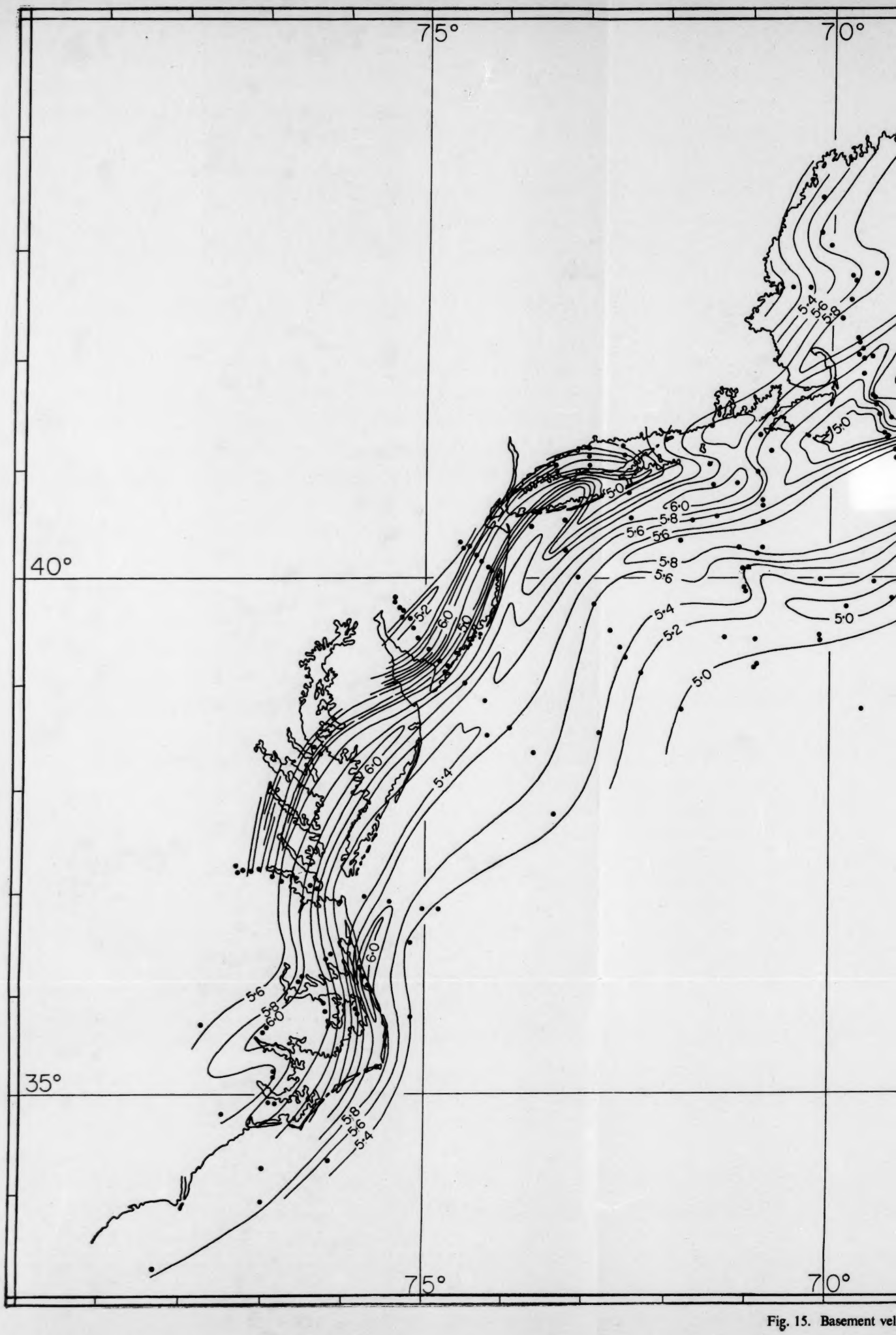
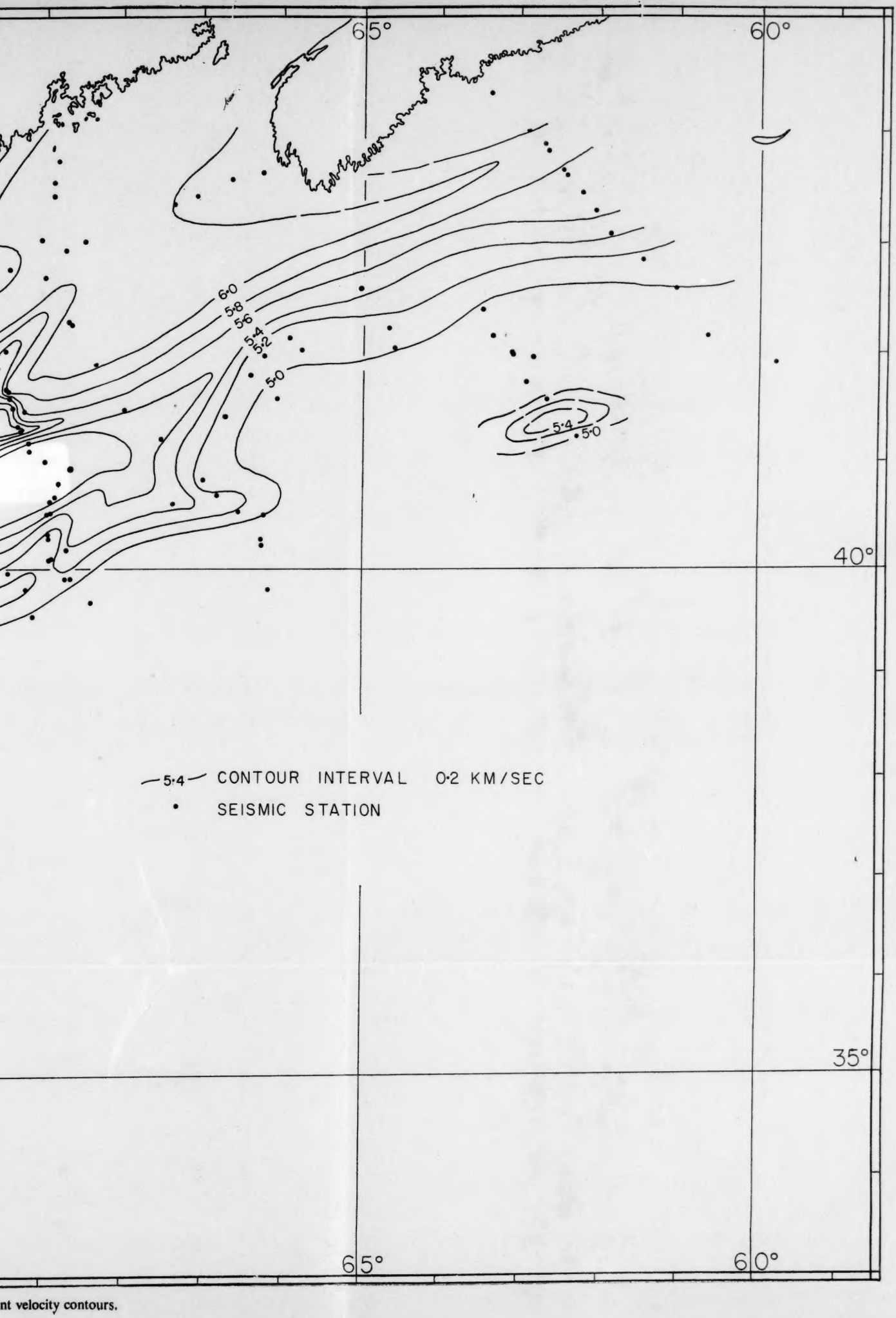


Fig. 15. Basement vel



nt velocity contours.

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One cause for the difficulty in establishing definite stratigraphic horizons arises from the sediments themselves. Rather than being continuous beds of the same material, they are quite variable and show great changes both laterally and vertically. Spangler and Peterson (1950) emphasize that the combination of marine and continental beds with limited lateral extent together with lack of definite ages and boundaries in many cases makes correlation difficult.

The velocity information, then, does not determine the stratigraphy of the coastal plain sediments but rather their degree of lithification. As a whole, they represent a more or less continuous sequence of variable lithology with only minor breaks.

Well logs indicate that the age of the sediments ranges from at least Jurassic to recent. Jurassic sediments have been found in wells south of this area and there is a possibility that arkosic sands and varicoloured shales found below − 9150 ft in the Hatteras well (Fig. 34, No. 103) are of this age. SPANGLER (1950) mentions that J. B. Reeside, Jr. considered a Pecten found at − 9115 ft as no younger than Lower Cretaceous nor older than Jurassic.

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No positive evidence has been found, to date, that Triassic sediments are part of this sequence. All known Triassic sediments in this area have been found in fault basins. OFFICER and EWING (1954) have suggested that the great thickness of "consolidated sediments" found on the Halifax profile are of probable Triassic age. Similarly EWING *et al.* (1950) discuss the possibility of Triassic sediments off New Jersey. It is entirely possible that Triassic (or even older) sediments are present near the base of the sedimentary column but their presence cannot be verified by the velocity data.

Continental Crust

Identification of the continental crustal layer as differentiated from the other layers is possible due to the abundance and closeness of the profiles. For brevity, this layer will be referred to as "basement" since, where identified by the drill, it corresponds to this term as generally used by geologists. The basement surface is traced from profile to profile on the basis of its depth. Examination of the sections of Fig. 35 will show the justification for this.

As the depth to basement decreases, more and closer-spaced variations in the velocities are evident. This is to be expected since the shallower profiles are shorter and do not average so long a section of the basement rocks. They will be more influenced by local changes in lithology and structure. The longer profiles will give an average velocity in a suite of basement rocks and local variations, minimized to some degree by the pressure of the overburden, will show up as scatter of the points. Variations in velocities between these long profiles reflect regional rather than local differences in geology.

Variations in the basement velocity were examined in the earlier papers of this series, but the data were too limited to allow close correlation with the regional geology. Woollard (EWING *et al.*, 1940, pp. 1834–1836) showed that the variation of velocity along the Cape Henry line appeared to be the same as that of the New Jersey coastal plain and suggested lithologic control as the cause. OFFICER and EWING (1954) noticed a decrease in basement velocity seaward on the profiles in the Nova Scotia area. Two possibilities were suggested: (1) there is a decrease of metamorphism under the continental rise farther from the main orogenic belt, or (2) the lower velocities represent Paleozoic sediments

deposited seaward from a source on the outer part of the continental shelf while the great thicknesses of sediment were being deposited landward in the Appalachian geosyncline. A lack of variation of the basement velocity was noted in the Gulf of Maine (DRAKE *et al.*, 1954) and the basement was divided into two layers; an upper "granitic" layer (5 + km/sec) corresponding to the late Paleozoic intrusives and metamorphics of the area, and limited to the margins of the Gulf and a lower layer (6 km/sec) representing the older crustal material beneath this.

In order to see if the basement velocities vary systematically over the whole area under consideration, their values were plotted on a map and velocity

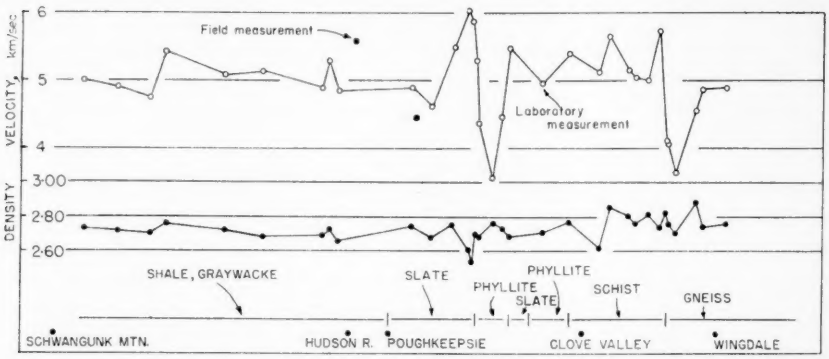

Fig. 16. Seismic velocities and densities of progressively metamorphosed rocks from locations between Schwangunk Mountain, Orange County and Wingdale, Dutchess County, N.Y.

contours were drawn at intervals of 0·2 km/sec. Two major trends are revealed by these contours (Fig. 15); a pattern of alternating higher and lower velocities paralleling Appalachian structure, and a general decrease in the velocity seawards.

The factors responsible for velocity variations in general must be clearly understood if we are to find the cause of this regular pattern. For crustal rocks at relatively shallow depths the two most important factors are porosity, as represented by interstices, cracks, cleavage, or other voids, and composition.

For most common sedimentary and parametamorphic rocks porosity is the more significant of these two. It has been shown (NAFE and DRAKE, 1957) that, for sedimentary rocks, porosity may be predicted within rather narrow limits from compressional velocity alone. Since the parametamorphic rocks are produced from the sediments without gross changes in the overall chemical composition, velocities in these rocks should behave in the same manner. This is verified by velocity–density relationships reported in the above paper and by velocity measurements on samples of rock from Dutchess and Ulster Counties, New York. These samples are from an area studied by BALK (1936, pp. 685–774) and BARTH (1936, p. 775–850), are progressively metamorphosed, and range from shales and graywackes on the west to gneisses on the east. The overall chemical composition changes remarkably little over this metamorphic range.

The mean velocity in the sedimentary rocks is approximately equal to that in the metamorphics but there is considerably more variation in the latter group (Fig. 16). The values for slate are high since they are measured in single slabs.

In the field these values will be reduced somewhat when many slabs must be crossed. The phyllite values are probably somewhat lower than field measurements would produce due to poor coupling of the irregular plates in the sample measured at atmospheric pressure. The velocities in the more massive sediments vary with density and it is likely that the *in situ* values of the metamorphics would behave in the same manner. Since there is a slight increase in the average density of the more highly metamorphosed rocks, it might be expected that there would be a slight increase in velocity.

Composition should be a more important factor in determining the velocity in igneous or orthometamorphic rocks. It is well known that there is a general increase in velocity as rocks become more basic and denser. This is illustrated by the velocity–density relationships observed in Fig. 25. This effect is much more important in the velocity range above 6 km/sec than in that below, but it must be considered if proper correlations between geology and velocity are to be made.

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An examination of the geological data from the high basement velocity areas fails to reveal a systematic correlation with composition. In the Gulf of Maine, where the basement velocity is uniformly about 6 km/sec, there are no surface outcrops, but R. S. Edwards of the Woods Hole Oceanographic Institution collected a sample of rock from Cashe's Ledge, a shoal area near the centre of the Gulf, which has been identified as a quartz monzonite. A sample of basement rock from the Hatteras well (Fig. 34, No. 108), where the velocity is about 5·8 km/sec, is of the same material. Dr. Jasper L. Stuckey, State Geologist of North Carolina (personal communication), has made a field identification of the basement rock from the Havelock well (Fig. 34, No. 113) as quartz–biotite gneiss. The basement velocity here is 6·08 km/sec. W. Bonini of Princeton University and others have worked to the south of this area and found that the velocities in the granite–gneiss–schist group reach higher values than do those of the volcanic slates.

It would appear, then, that we must look for a structural rather than a compositional explanation for the velocity changes. Furthermore, since the velocity trends are consistent over large areas and parallel Appalachian trends, we must look for major features related in some manner to the deformation of this system.

Several possibilities present themselves. Since the Pre-Cambrian rocks have been subjected not only to Paleozoic metamorphic processes but to earlier ones as well, they should have reached a higher degree of metamorphism with accompanying decrease in pore space and increase in velocity. The fact that they were buried beneath the Paleozoics should add to this effect. Furthermore, since they have been in existence for a longer period of time, there has been more opportunity for cementation and pore filling to take place.

An alternative possibility is that the high velocity (5·8–6·0 km/sec) regions are metamorphic centres of different periods of activity. The major influence of the Acadian orogeny, for example, is somewhat to the east of that of the earlier Taconic orogeny. It is possible that its influence south of New England was principally under the present continental shelf and that the axis of major deformation and intrusion is marked by the high velocity regions (Fig. 15).

The structural relationships in the Gulf of Maine favour the former explanation, that the high velocities represent older rocks. The upper layer here, as mentioned before, correlates with the Paleozoic intrusive and stratified rocks of

New England and Nova Scotia. The profile closest to Cape Ann, Mass., has a basement velocity of 5·06 km/sec as compared with 5·34 km/sec for Rockport granite from this area. The profile closest to Portland, Maine, where Paleozoics are also found at the surface, has a basement velocity of 5·49 km/sec as compared with the value of 5·34 km/sec obtained by KATZ *et al.* (1953) for a long profile shot in the Gulf but recorded on land. The dip of this layer is well determined under Profile LRB 43–40 (Fig. 1). A projection of this dip shorewards results in a depth to the higher velocity layer beneath in very good agreement with that determined by Katz. Profile PR6, closest to Matinicus Rock, does not indicate the presence of the upper layer. This is not in disagreement with the results of Katz which indicate that the depth to the high velocity layer under Mt. Desert Island, some 30 miles north, is considerably less than at Portland.

The two profiles closest to Yarmouth, Nova Scotia, show the same layering with the upper layer resting in a trough-like feature reaching a maximum thickness of about three kilometres about 40 miles offshore and pinching out to the west and thinning to 1 km near the coast. The above interpretation of these layers is not incompatible with the geology of southwestern Nova Scotia.

Table 2. Seismic Compressional Velocities Compared with Basement Lithology from Adjacent Wells

Location	Velocity (km/sec)	Rock type
Block Island, R.I.	5·8	"Granite"
Orient Point, N.Y.	5·4	Schist
Greenport, N.Y.	5·2	Schist
Long Beach, N.Y.	5·7	Granite gneiss
Coney Island, N.Y.	5·1	Granite
Rockaway Pt., N.Y.	5·4	Medium gray granite
Hightstown, N.J.	5·6	Wissahickon gneiss
Jackson Mills, N.J.	4·9	Wissahickon schist
Salisbury, Md.	5·9	Triassic sediments, granite, gneiss
Mathews, Va.	6·0	"Granite"
Foreman No. 1, N.C.	5·8	Triassic sediments and diabase
Hatteras, N.C.	5·8	Quartz monzonite
Havelock, N.C.	6·1	Quartz–biotite gneiss
Folkstone, N.C.	5·9	Quartz–biotite schist

While the evidence from the Gulf of Maine points to an upper layer of Paleozoic metamorphics and intrusives underlain by Pre-Cambrian basement with a higher seismic compressional velocity, it is difficult to carry this relationship to the south. The basement rocks here are covered by water or coastal plain sediments and revealed only by scattered wells (Table II) and in the great majority of cases only a single basement layer is encountered. The only conclusion which may be drawn is that there is a gneiss–granite group which has higher velocities than another group made up of such rocks as the volcanic slates of the Carolinas and Georgia, the Wissahickon schist, the metamorphics of the New York City area, and others.

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Present geological thought assigns a Paleozoic age to the latter group. BALK (1936) identifies the New York group with the less metamorphosed Cambro-Ordovician rocks of Dutchess and Ulster Counties to the north. PAIGE (1956, pp. 391–394) has shown that these rocks are identical in Rockland and Westchester Counties. CLOOS and HIETANEN (1941), from studies in Pennsylvania and Maryland, have concluded that the Glenarm (of which the Wissahickon is a member) cannot be Pre-Cambrian. Lombard (1948) observed that the Piedmont area seems to belong partly to a narrow geosynclinal belt of mobile character and partly to a cratonic unit acting as a hinterland during the Appalachian orogeny and puts the Glenarm in the geosynclinal part of it. Recent age determinations are further limiting the extent of the Pre-Cambrian rocks, the major outcrops being well over on the west side of the Piedmont. This is most logical since, if the Piedmont is to be considered an eugeosynclinal trough intruded and metamorphosed, one would expect to find Pre-Cambrian basement rocks on the flanks of the trough rather than in the centre.

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It is not out of order to conclude, then, that the high velocities represent the basement rocks under the Paleozoics on the east side of this trough. Such an explanation would not, however, account for the repeated pattern. This may be due to Acadian or later activity. The Pre-Cambrian axis mentioned above swings north in the vicinity of New York City and extends into Vermont. Exposures of Pre-Cambrian to the east of this axis are rare until one reaches eastern Maine and the Maritime Provinces. In the latter area the Green Head, George River, and Coldbrook groups are known definitely to be Pre-Cambrian (EARDLEY, 1951, p. 174) while others, including the Meguma and the Macquereau have been regarded as Pre-Cambrian in the past on less satisfactory evidence. The recent discovery of Ordovician fossils in the Meguma series places it definitely in the Paleozoic. There is, then, another axis of Pre-Cambrian rocks extending through New Brunswick which may be projected into western Newfoundland. In eastern Newfoundland there is still another Pre-Cambrian axis seawards from the above. To these recurring axes may be attributed the high velocity bands.

The two possibilities suggested by OFFICER and EWING (1954) to explain the systematic decrease in velocity seaward from the coast have been cited previously. These were a decrease in the intensity of the metamorphism and the presence of Paleozoic sediments. These two factors are not mutually exclusive since a sufficient decrease in the intensity of metamorphism would imply that sediments are present. It is possible to determine whether these are indeed the controlling factors by examining the data from wells drilled to basement under the coastal plain.

A large number of wells have been drilled to basement in the coastal plain between Rhode Island and Alabama but, unfortunately, the basement rocks are not described in detail for many of them. Such terms as "bedrock", "basement", "Pre-Cambrian", or "granite", the last having no petrological significance, are often used. The nature of the basement rocks has been described in more or less detail for a smaller number of deep wells (Table 3). There are sufficient of these that a general picture of the basement rocks can be obtained. In Table 3 and on the descriptive maps (Figs. 17–21) Triassic fault basin rocks have been included in the basement category.

The basement rocks of the Long Island–Block Island area (Fig. 17) are

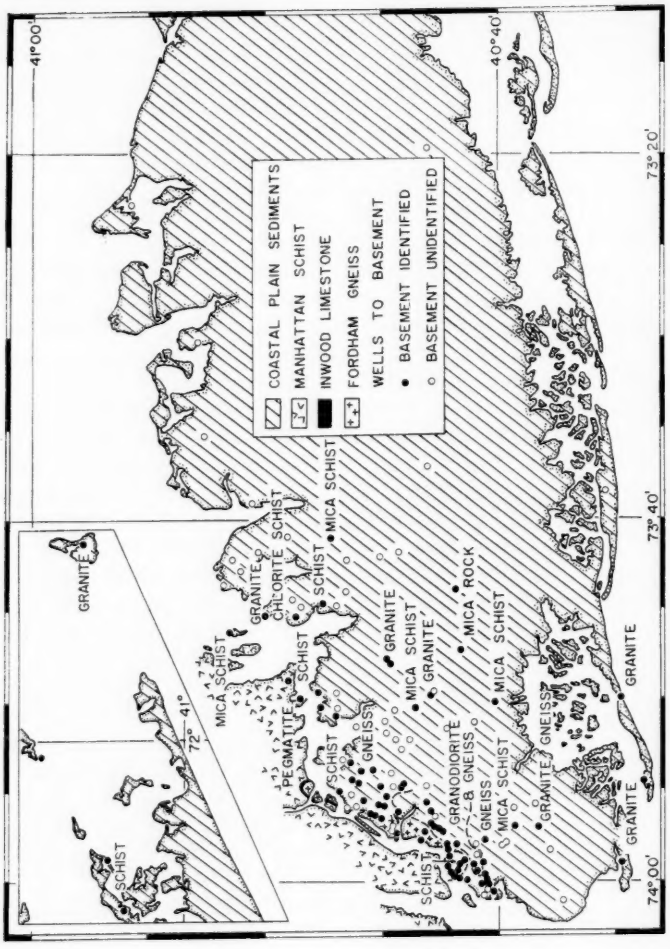

Fig. 17. Deep wells and generalized geology, Long Island, New York.

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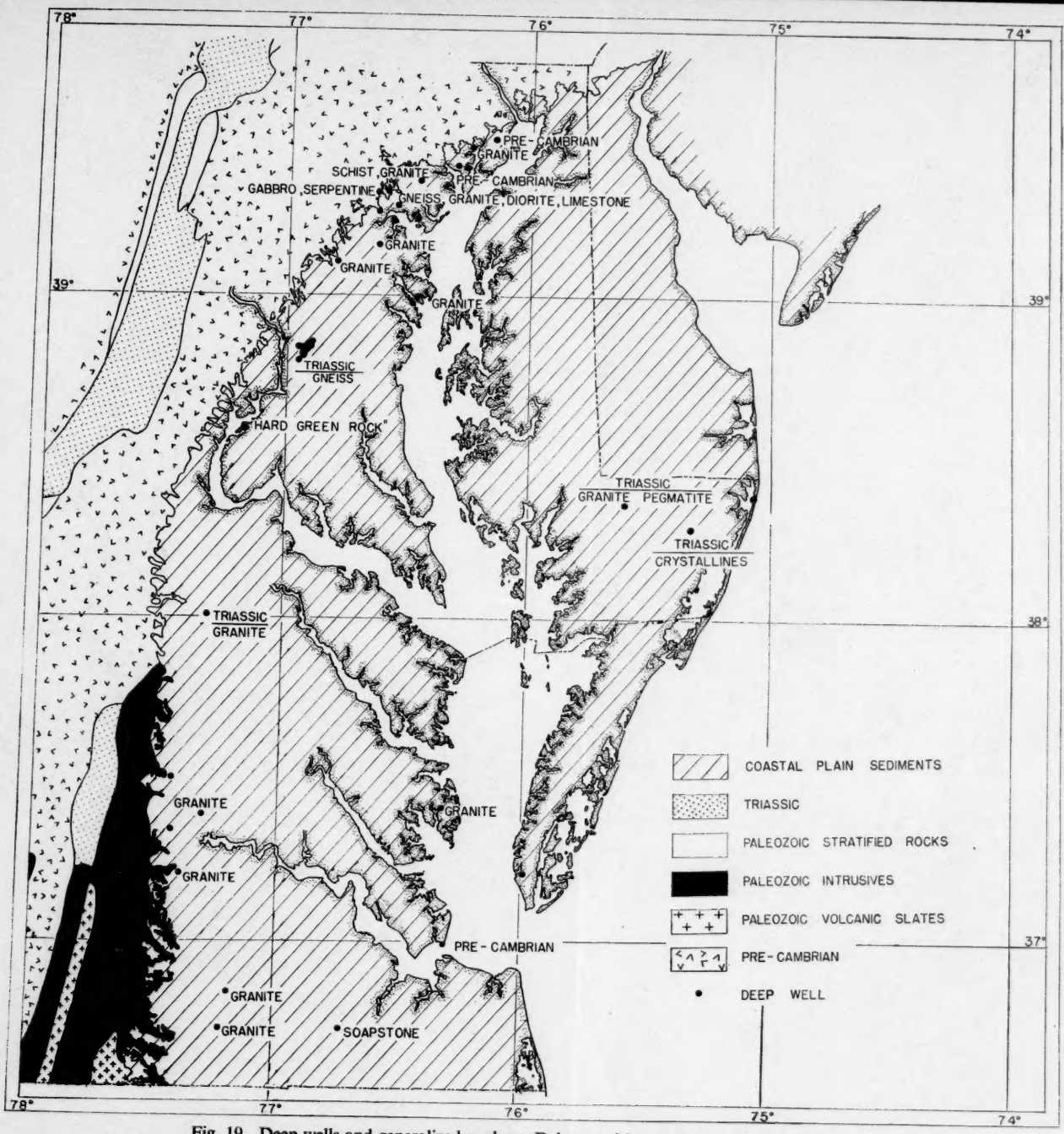

Fig. 19. Deep wells and generalized geology, Delaware, Maryland, and Virginia.

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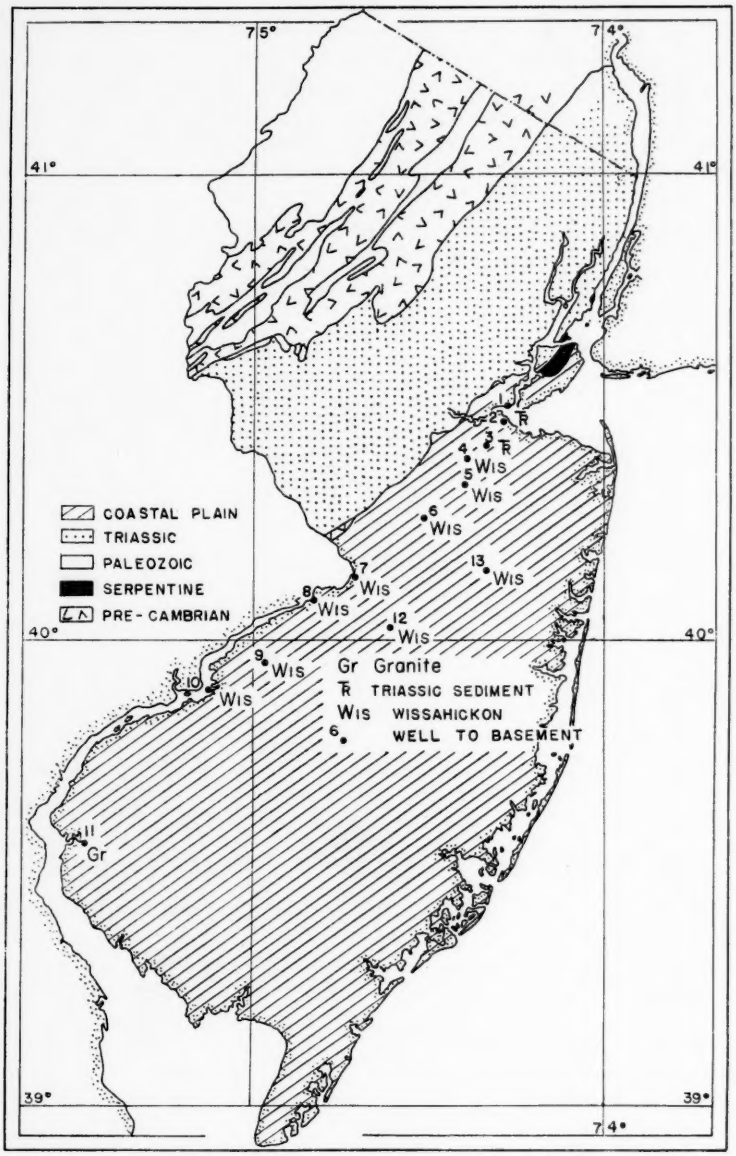

Fig. 18. Deep wells and generalized geology, New Jersey.

similar to those of Westchester County and Connecticut consisting principally of granites, gneisses and schists. The basement at Duck Island, off Northport (Fig. 34, No. 6) was reported to be "sandstone" but there is some doubt as to the integrity of the driller. No wells have been drilled to basement along the New Jersey shore (Fig. 18) and those farther inland mostly encountered Wissahickon schist. Buried Triassic sediments were reported from two wells in northern New Jersey (Fig. 34, Nos. 48, 50). The situation is much the same in Maryland and Virginia (Fig. 19). The basement rocks are crystalline, with a greater variety than reported to the north, and Triassic rocks were encountered in a number of wells. In North and South Carolina the volcanic slates indicate a somewhat lower degree of metamorphism (Fig. 20) but the well which is

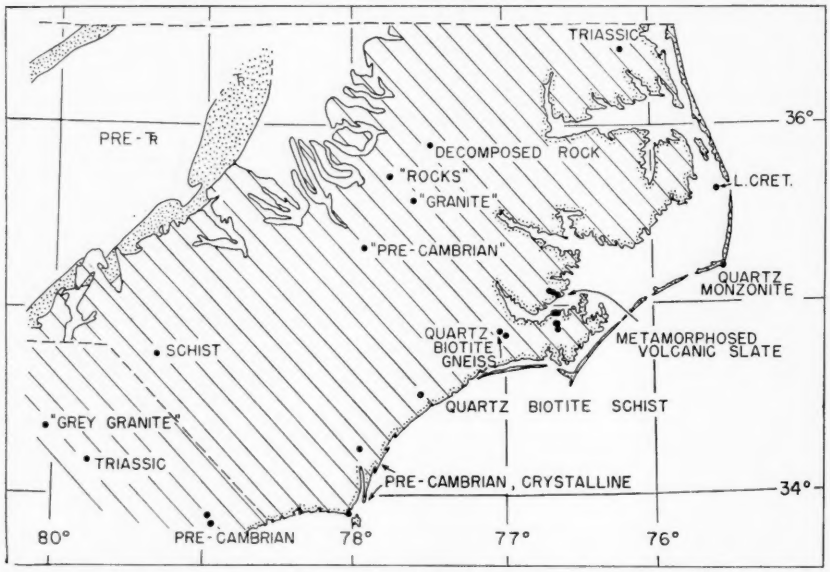

Fig. 20. Deep wells and generalized geology, eastern North Carolina.

closest to the edge of the shelf, at Cape Hatteras (Fig. 34, No. 103) bottomed in a quartz monzonite.

It is not until southern Georgia and Florida are reached that the rocks change appreciably in character. Here the picture becomes quite different. The Appalachian structures swing westward and since the oil possibilities have encouraged a great deal of exploratory drilling in this area, there are a great number of wells to basement which encounter rocks presumably equivalent to those under the submerged shelf to the north. The data from these wells has been accumulated and presented in a very significant report by P. L. APPLIN (1951). The distribution of the basement rocks presented in Fig. 21 is taken from Applin's report and the descriptions may be found in Table 2. It can be seen that there is a regular distribution of the three units. Crystalline rocks of the Piedmont province are found in southern Georgia and Alabama with Paleozoic sediments coming in near the Florida border and extending part way down the peninsula and with volcanics in the southern part of the peninsula. Some volcanics were

also found just north of the Paleozoic sediments in Georgia, and three wells in central Florida are reported to show intrusive rocks. One of these, No. H8, Fig. 21, has been reported as "granite?" but has not been studied petrographically; the other two, Nos. H6 and H9 were examined by F. F. Grout and identified as hornblende diorite and altered and veined biotite granite, and may be intrusive equivalents of the volcanics.

The Paleozoic rocks have been dated on the basis of fossils and range from at least early Ordovician to lower or possibly middle Devonian (BRIDGE and BERDAN, 1950).

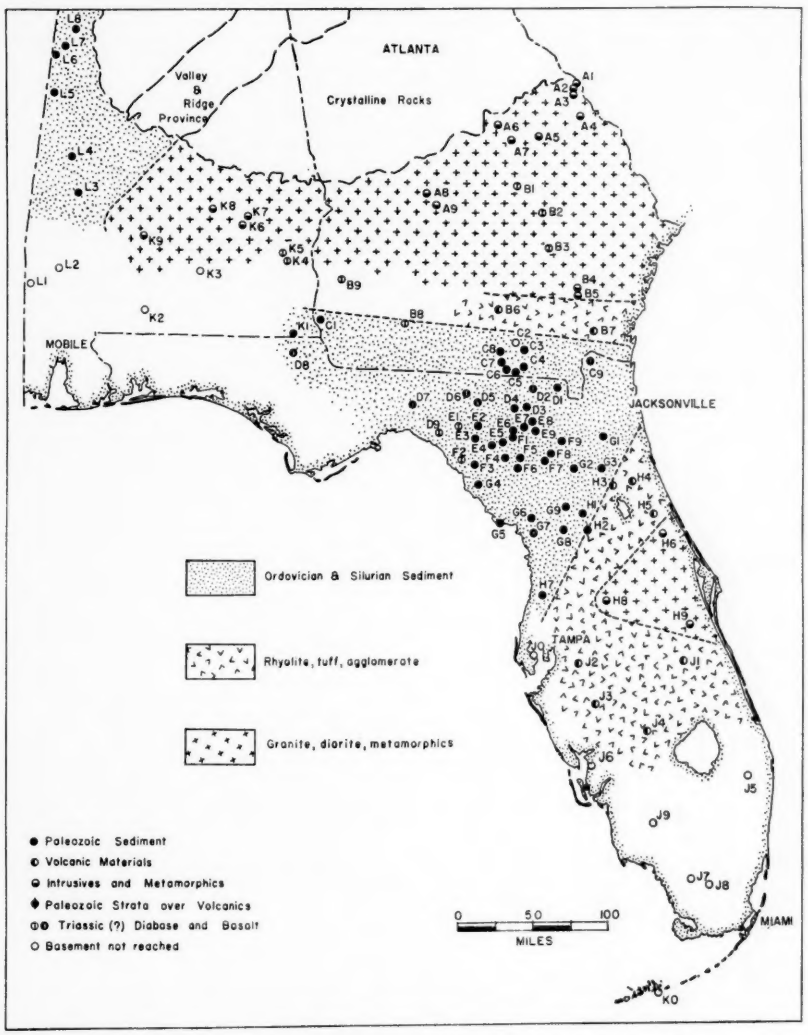

Fig. 21. Deep wells and generalized geology, Georgia, Florida, Alabama (after APPLIN, 1951).

Table 3. Wells to Basement and Other Significant Deep Wells in the Coastal Plain Between Rhode Island and Alabama

County	Well Description	No.	Date	Bedrock Elevation	Type of Rock	Ref.
Rhode Island						
Newport	Block Island Water Co.	1	1950	− 80	"Rotten granite that was all crumbled and looked like rotten rock"	1*
New York						
Suffolk	S189, Orient Point	2	1935	− 663	"Muscovite, chlorite, magnetite, clay, and a few pieces of decayed schist"	2
Suffolk	S420, Greenport	3		− 674	Schist	3
Suffolk	S6409, Brookhaven	4		− 1445	"Bedrock"	4
Suffolk	S6434, Brookhaven	5		− 1495	"Bedrock"	4
Suffolk	S34, Duck Island, off Northport	6		− 597	Reported as "sandstone" by driller	3
Nassau	N216, Hewlitt Point	7		− 225	"Soft gray granite and mica veins; same character as found throughout Westchester County, New York"	3
Nassau	N687, Great Neck	8	1939	− 310	Schist	3
Nassau	N1328, Manhasset	9	1941	− 559	Mica schist	3
Nassau	N1926, Kings Point	10	1943	− 246	Chlorite schist	3
Nassau	N1618, Manhasset	11	1941	− 491	"Clay, micaceous and decomposed rock"	5
Nassau	N1927, Long Beach	12	1943	− 1458	Probably granite gneiss	5
Queens	Q31, Glendale	13	1937	− 421	Mica schist	3
Queens	Q33, College Point	14	1934	− 179	Granite	3
Queens	Q262, Jackson Heights	15		− 123	Fordham gneiss	3
Queens	Q272, Forest Hills	16	1930	− 457	Granite	3
Queens	Q274, Flushing	17		− 387	Granite	3
Queens	Q283, Flushing	18		− 415	Granite	3
Queens	Q350, Ozone Park	19	1934	− 577	Mica schist	3
Queens	Q390, Long Island City	20		− 171	Fordham gneiss	3
Queens	Q393, Long Island City	21	1924	− 133	Fordham gneiss	3
Queens	Q403, Rockaway Point	22	1914	− 865	Granite	3
Queens	Q433, Maspeth	23	1924	− 146	Fordham gneiss	3
Queens	Q435, Maspeth	24	1923	− 176	Fordham gneiss	3
Queens	Q436, Maspeth	25	1923	− 187	Gneiss and granodiorite	3

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Queens	Q437, Maspeth	26		− 207	Fordham gneiss	3
Queens	Q438, Maspeth	27	1923	− 184	Fordham gneiss	3
Queens	Q562, Jamaica	28	1935	− 649	"Mica rock"	3
Queens	Q568, St. Albans	29	1933	− 811	"Mica rock"	3
Queens	Q1030, Rockaway Park	30	1939	− 975	"A medium gray, even textured granite in which pink and gray feldspar and glassy quartz are easily discernible to the eye . . . small flakes of muscovite, biotite, and other mica-like minerals, a few small red garnets . . . no evidence of regional metamorphism was found. . . ."	6
Queens	Q1353, Whitestone	31		− 142	Mica schist	3
Kings	K1, Coney Island	32		− 625	Granite	3
Kings	K532, Flatbush	33	1930	− 409	Granite	3
Kings	K534, Flatbush	34	1915	− 404	Gneiss	3
Kings	K655, Brooklyn	35	1924	− 148	Gneiss	3
Kings	K663, Brooklyn	36	1924	− 161	Granodiorite	3
Kings	K664, Williamsburg	37	1924	− 142	Granodiorite	3
Kings	K665, Williamsburg	38	1924	− 140	Granodiorite	3
Kings	K672, Williamsburg	39	1923	− 131	Granodiorite	3
Kings	K673, Williamsburg	40	1923	− 162	Gneiss and granodiorite	3
Kings	K675, Williamsburg	41	1923	− 190	Gneiss and granodiorite	3
Kings	K677, Williamsburg	42	1923	− 177	Gneiss and granodiorite	3
Kings	K678, Williamsburg	43	1923	− 161	Gneiss and granodiorite	3
Kings	K690, Greenpoint	44	1927	− 161	Granodiorite	3
Kings	K691, Williamsburg	45	1927	− 122	Granodiorite	3
Kings	K731, Brooklyn	46	1927	− 160	Gneiss	3
New Jersey						
Middlesex	Perth Amboy	47		− 130	Metamorphosed Triassic shale	7
Middlesex	South Amboy	48		− 320	Triassic red shale	7
Middlesex	Runyon	49		− 300	"Three feet of red shale, then very hard gray rock"	7
Middlesex	Dunhams Corners	50	1928	− 170	Triassic red shale	8
Middlesex	East Spotswood	51		− 270	Wissahickon schist	7
Middlesex	Jamesburg, 3 miles east of	52		− 403	Pre-Cambrian gneiss	7
Mercer	Hightstown	53		− 374	Wissahickon gneiss	7

* These numbers refer to the reference list appearing at the end of Table 3 on p. 164.

Table 3—continued

County	Well Description	No.	Date	Bedrock Elevation	Type of Rock	Ref.
New Jersey (contd.)						
Mercer	Bordentown	54		− 217	Wissahickon schist	7
Burlington	Moorestown	55		− 498	Wissahickon schist	7
Burlington	Burlington	56		− 95	Wissahickon schist	7
Camden	Gloucester	57		− 256	Wissahickon schist	7
Salem	Salem	58		− 1364	Weathered granite	7
Burlington	Wrightstown	59		− 975	Wissahickon schist	7
Ocean	Jacksons Mills	60	1921	− 1226	Wissahickon schist	7
Delaware						
Sussex	Bridgeville, 4 miles SE of	61	1935		Bottomed in Cretaceous at − 2965	8
Maryland						
Baltimore	Sparrows Point	62		− 485	"Crystalline rocks, granite"	9
Baltimore	Baltimore	63			Numerous wells have been drilled to basement within the Baltimore city limits. These have encountered variously granite, limestone, gneiss, pegmatite, hornblendite, diorite, schist, gabbro, and serpentine.	10
Prince Georges	Bd-14, Linthicum	64		− 78	Gneiss	11
Prince Georges	Bd-18,	65		− 147	Gneiss, blue	11
Prince Georges	Cc-5	66		− 127	"Granite, 35 per cent milky quartz grains, also milky quartz"	11
Prince Georges	Cc-16	67		− 227	"Granite"	11
Ann Arundel	Ad-29	68		− 463	"Sandstone changing to rotten granite and getting harder and slower to drill"	13
Ann Arundel	Df-16	69		− 570	"Granite"	13
Prince Georges	Meadows, 1 mile S of	70			Bottomed in Patuxent at − 1254	8
Prince Georges	Fort Washington	71			Bottomed in Lower Cretaceous at − 880	8
Prince Georges	Wash. Gas Light Co., Buckler No. 2	72	1956		"Bottomed in sand above the Triassic" at − 1445.	12

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Prince Georges	W.G.L.Co., Butler No. 2	73	1956	— 1447	1447–1490, "Triassic clay" 1490–1550, "metamorphics, probably Pre-Cambrian basement gneiss"	12
Prince Georges	W.G.L.Co., Dennison No. 3	74	1956	— 1484	"Metamorphics, probably basement Pre-Cambrian gneiss"	12
Prince Georges	W.G.L.Co., Hill No. 1	75	1956	— 1335	"Triassic clay"	12
Prince Georges	W.G.L.Co., McMains No. 1	76	1956	— 1378	"Triassic arkose, silty and shaly to sandy and gravelly"	12
Prince Georges	W.G.L.Co., P. Moore No. 2	77	1956	— 1312	"Triassic clay"	12
Prince Georges	W.G.L.Co., P. Moore No. 3	78	1956		Bottomed in Patuxent at — 1089	12
Prince Georges	W.G.L.Co., Mudd No. 3	79	1956	— 1465	"Triassic conglomerate, sandstone, siltstone and shale"	12
Prince Georges	W.G.L.Co., Roberts No. 2	80	1956	— 1503	"Triassic clay with little sand"	12
Prince Georges	W.G.L.Co., Robinson No. 2	81	1956	— 1577	"Triassic mudstone"	12
Prince Georges	W.G.L.Co., Thorne No. 2	82	1956	— 1373	"Metamorphics, probably basement Pre-Cambrian gneiss"	12
Prince Georges	W.G.L.Co., Wedding No. 2	83	1956		Bottomed in Patuxent at — 1527	12
Charles	Indian Point	84		— 709	"Hard green rock" over "hard red rock" at — 891. Triassic?	14
Wicomico	Ohio Co., Hammond No. 1, Salisbury	85	1945	— 5303	5303–5472, Triassic, Newark: "similar to outcrops of the Newark series in Pennsylvania and New Jersey" 5472–5511, Pre-Cambrian basement complex including: 5472, medium grained crystalline rock injected with granite 5479, fine grained crystalline rock composed dominantly of ferromagnesian and plagioclase feldspar minerals. Hand specimen is light coloured, granitic in appearance, and shot through with veins of calcite 5485, same as 5472 with calcite veins 5485–5490, the upper specimen looks much like the Baltimore gneiss; the middle specimen seems more metamorphosed, garnet, calcite veins: the lower specimen contains no mafic minerals in thin section, granitic	15

Table 3—continued

County	Well Description	No.	Date	Bedrock Elevation	Type of Rock	Ref.
Maryland (contd.)						
Worcester	Socony-Vacuum, James D. Bethards No. 1	86	1945	− 6527	Triassic; conglomerate at base, coarse to fine grained sandstone above, predominantly shale in upper portion.	16
Worcester	Esso Standard, Maryland Esso No. 1	87	1946		Bottomed in Patuxent at − 7710	16
Virginia						
Caroline	Bowling Green	88		− 318	318–945, Triassic sandstone and clay 945–1335, "Pre-Cambrian, granite and sandstone"	17
Mathews	Mathews, Phillips Oil Co.	89		− 2292	2292, sand, grading down into red-yellow arkose. 2298, broken rock, arkosic, "just above granite" 2303, basal conglomerate 2305, granite	8
Chesterfield	Bensley	90		− 100	"Granite"	18
Chesterfield	Chester	91		− 115	115, light "granite" and flint 165, sandstone 167, fine gray sand 200, "soft white granite" 323, "white granite" 327, "hard gray granite"	18
Henrico	Curle's Neck	92		− 281	"Granite"	19
Dinwiddie	Petersburg, 2½ miles W of	93		− 220	220, "soft fissured granite" 312, "hard, solid, and fissured granite" 368, "hard granite"	18
Dinwiddie	Petersburg, 3 miles S of	94		− 178	178, "rotten granite" 700, "gray and brown granite"	18
Northampton	Cape Charles	95			Bottomed in Cretaceous at − 1790	16
Elizabeth City	North End Point	96			"Hardest kind of stone or granite" drill rods broke and work was abandoned at − 1170. Probably not basement	19

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Elizabeth City	Fortress Monroe	97	1902	− 2240	"Pre-Cambrian", "granite", "crystalline"	18
Sussex	Jarratt	98		− 180	"Granite"	18
Sussex	Grizzard	99		− 113	"Granite"	18
Southampton	Sedley	100		− 596	596, soapstone 633, green sandy soapstone and soft brown clay	18
North Carolina						
Camden	du Grandlee, Foreman No. 1, 4 miles NE of Elizabeth City	101	1953	− 3490	2850–3490, greenish cherty limestone and dolomite (Lower Cretaceous or Jurassic) not in Hatteras well 3490–4880, Triassic, reddish carbonaceous shale, some sand 4880–5020, Triassic, fresh diabase with smoky augite, calcic plagioclase, some hypersthene 5020–5360, Triassic, reddish shale, black diabase, greenish calcerous chert 5360–5470, Triassic, mixed sediment and diabase (very contaminated) 5470–6391, quartz sand, quartzite	20
Dare	Esso Standard, N. Car. Esso No. 2	102	1947		Bottomed in Lower Cretaceous at − 6410	21
Dare	Esso Standard, Hatteras No. 1	103	1946	− 9853	Weathered granitoid igneous rock, some schistosity. Primary minerals orthoclase, oligoclase, microcline, quartz. Complete absence of ferromagnesian minerals. Quartz monzonite, later sheared to form flaser quartz monzonite	21
Cartaret	Car. Pet. Co., Guy M. Carraway No. 1	104	1946	− 4035		
Cartaret	Car. Pet. Co., Nita Carraway No. 1	105	1946	− 4100		
Cartaret	Car. Pet. Co., D. L. Philips No. 1	106	1946	− 3915		
Cartaret	Car. Pet. Co., H. B. Salter No. 1	107	1946	− 3935	One or two of these wells bottomed in a metamorphosed material very similar to the rocks of the volcanic slate belt of the Piedmont of North Carolina	21, 22
Cartaret	Car. Pet. Co., John Wallace No. 1	108	1946	− 4081		
Pamlico	Car. Pet. Co., N. Carolina Pulpwood No. 1	109	1947	− 2393		
Pamlico	Car. Pet. Co., Atlas Plywood No. 1	110	1947	− 3395		
Pamlico	Car. Pet. Co., Lindley No. 1	111	1947	− 3175		
Craven	Car. Pet. Co., Charles Bryan No. 1	112	1947	− 2393		
Craven	Havelock, Great Lakes Drilling Co.	113	1926	− 2288	Quartz-biotite gneiss	21, 22
Cartaret	Morehead City, Coastal Plains Co., F. L. Karston, Laughton No. 1	114		− 4013	"Basement"	21

Table 3—continued

County	Well Description	No.	Date	Bedrock Elevation	Type of Rock	Ref.
North Carolina (contd.)						
Onslow	Folkstone, Cadco No. 1	115	1950	− 1449	Quartz-biotite schist	22
Edgecombe	Tarboro	116		− 278	"Decomposed rock"	16
Wilson	Wilson	117		− 122	"Rocks"	16
Pitt	Farmville	118		− 385	"Granite"	16
Wayne	Goldsboro, Seymour Johnson Air Field	119		− 116	"Pre-Cambrian" basement rock	16
New Hanover	Wilmington, Clarendon Water Works	120		− 1100	"Pre-Cambrian, crystalline"	16
New Hanover	Fort Caswell	121		− 1530	"Pre-Cambrian, crystalline"	22
Scotland	Maxton Glider Base	122		− 153	Schist, "Pre-Cambrian"	16
South Carolina						
Horry	Allsbrooks, Palmetto Drilling Co.	123	1939	− 1043	"Bedrock"	16
Horry	Conway, Hucks No. 1	124		− 1350	"Pre-Cambrian"	16
Horry	Smart Farm, Pioneer Oil Co.	125		− 1369	"Pre-Cambrian", bedrock	16
Florence	Florence	126		− 461	461–1193, Triassic? sandstone 1193, "black rock", "dike?"	16
Darlington	Hartsville	127		− 488	"Gray granite"	23
Dorchester	Summerville	128		− 1542	1542, Triassic? coarse reddish sand, greenish clay and pyrite 1574, diabase 1931, reddish shale and sandstone, poorly rounded pebbles at base 2379, chiefly pinkish sand and gravel; gray clay from bit at 2122, red clay at 2137 2399, diabase (After COOKE, 1936, and MUNYAN, 1943: RICHARDS, 1945 and MANSFIELD, 1937, consider this section to be Cretaceous)	16, 23
Charleston	Charleston	129			Bottomed in Upper Cretaceous (Black Creek) at − 2005	16
Beaufort	Parris Island, Marine Base	130			Bottomed in Upper Cretaceous (Tuscaloosa) at − 3436	16

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Georgia						
Richmond	Circular Court	A1		− 19	Talcose schist	24
Richmond	Allens Station, Three Creeks Oil Co.	A2	1921	?	"Crystalline rock"	24
Richmond	Gracewood, Ga. Trng. Sch.	A3		− 189	Talcose schist	24
Burke	Green Cut, Three Creeks Oil Co.	A4	1923	?	"Crystalline rock"	24
Jefferson	Louisville, A. F. Lucas and Ga. Pet. Co.	A5	1907	?	"Crystalline rock"	24
Washington	Tennile, Layne-Atlantic's N.S.C. water well	A6	1945	− 411	"Granite"	24
Washington	Sandersville, 12 miles N of Mid. Ga. Oil. and Gas. Co.	A7	1920	?	"Crystalline rock"	24
Houston	Tricon Minerals Inc., J. D. Duke No. 1	A8	1949	− 1071	Biotite gneiss	24
Houston	Tricon Minerals Inc., H. B. Gilbert No. 1	A9	1949	− 1318	Biotite gneiss	24
Laurens	Minter, Calaphor Mfg. Co., Grace McCain No. 1	B1	1945	− 2252	Triassic? diabase under Lower Cretaceous or older Mesozoic	24
Montgomery	Higgston, J. E. Weatherford, Lonnie Wilkes No. 1	B2	1946	− 3122	Triassic? diabase under Lower Cretaceous or older Mesozoic	
Appling	Fesenthal and Weatherford, Mrs. W. E. Bradley No. 1	B3	1947	− 3866	Triassic? altered amygdaloidal basalt, probably a lava flow; under Lower Cretaceous or older Mesozoic	24
Pierce	W. B. Hinton, Adams–McCaskill No. 1	B4	1934	− 4273	Granite, pink	24
Pierce	Pan-Am. Prod. Co., Adams–McCaskill No. 1	B5	1938	− 4270	Granite	24
Atkinson	Sun Oil, Doster Ladson No. 1	B6	1945	− 3998	Volcanic tuff or agglomerate composed of hydrothermally altered rhyolite	24
Camden	Cal. Co. John A. Buie No. 1	B7	1948	− 4609	Volcanic ash and rhyolitic tuff	24
Mitchell	Stanolind, J. H. Pullen No. 1	B8	1944	− 6212	Diabase sills or dikes in Triassic? clastics	24
Calhoun	Sowega Min. Expl. Co., J. W. West No. 1	B9	1950	− 4845	Triassic? diabase under Lower Cretaceous or older Mesozoic	24
Early	Mont Warren *et al.*, A. C. Chandler No. 1	C1	1943	− 6763	6763–7053, black shale 7053–7133, quartzitic sandstone	24
Clinch	Sun Oil, W. J. Barlow No. 1	C2	1947		Bottomed in Lower Cretaceous at − 3670	24
Clinch	Hunt Oil, Alice Musgrove No. 1	C3	1944	− 3806	Black shale	24
Echols	Hunt Oil, Sup. Pine Prod. No. 2	C4	1945	− 3588	Quartzitic sandstone	24
Echols	Hunt Oil, Sup. Pine Prod. No. 3	C5	1947	− 3514	3514–3592, weathered zone? 3592–3860, black shale	24
Echols	Hunt Oil, Sup. Pine. Prod. No. 1	C6	1944	− 3634	Black shale	24

Table 3—continued

County	Well Description	No.	Date	Bedrock Elevation	Type of Rock	Ref.
Georgia (contd.)						
Echols	Hunt Oil, Sup. Pine Prod. No. 4	C7	1948	– 3755	Red micaceous silty shale, weathered?	24
Echols	Humble, Bennett and Langdale No. 1	C8	1949	– 3927	Sandstone and shale. 3944–3969, Triassic? dike or sill	24
Florida						
Nassau	St. Mary's River Oil Co., Hilliard Turpentine No. 1	C9	1940	– 4530	168 ft of black shale over diabase. Shale has been assigned variously to Triassic, Miss., Penn., or older	24
Baker	Hunt Oil, H. L. Hunt No. 1	D1	1947	– 3212	Quartzitic sandstone	24
Columbia	Humble, J. P. Cone No. 1	D2	1948	– 3341	3341–3351, weathered zone? 3351–4303, black shale (six Triassic? diabase and amygdular basalt sills from 1–33 feet in thickness included in section)	24
Columbia	Sun Oil, M. W. Sapp No. 1A	D3	1948	– 3165	Black shale	24
Suwannee	Sun Oil, J. H. Tillis No. 1	D4	1947	– 3338	Black shale	24
Madison	Hunt Oil, J. W. Gibson No. 4	D5	1945	– 3987	Quartzitic sandstone and shale	24
Madison	Hunt Oil, J. W. Gibson No. 2	D6	1944	– 4521	Black shale	24
Jefferson	Coastal Pet. Co., E. P. Larsh No. 1	D7	1949	– 7858	Quartzitic sandstone, possibly Paleozoic	24
Jackson	Humble, C. W. Tindel No. 1	D8	1949	– 8312	Red and gray sandstone and shale; porphyritic hornblende basalt from 8762–8804; basalt from 8842–8855	24
Taylor	Humble, G. W. Hodges No. 1	D9	1948	– 6117	6117–6129, basaltic rock, under Triassic? or Jurassic? clastics 6129–6218, diabase gabbro	24
Taylor	Gulf, Brooks–Scanlon No. 1	E1	1949	– 5104	Diabase gabbro under Triassic? or Jurassic? clastics	24
Lafayette	Humble, R. L. Henderson No. 1	E2	1948	– 4153	Quartzitic sandstone and shale	24
Lafayette	Gulf, Brooks-Scanlon No. 1	E3	1949	– 4418	Quartzitic sandstone	24
Lafayette	Sun, P. C. Crapps No. 1	E4	1946	– 3960	Quartzitic sandstone and shale	24
Lafayette	Coastal Pet. Co., R. Sapp No. 1	E5	1949	– 3435	Quartzitic sandstone and shale	24
Suwannee	Sun, A. B. Russell	E6	1949	– 3040	Quartzitic sandstone	24
Columbia	Sun, W. F. Johnston No. 1	E7	1949	– 2946	Quartzitic sandstone	24

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Columbia	Sun, Ruth M. Bishop No. 1	E8	1949	— 2639	Quartzitic sandstone and shale	24
Columbia	Sun, Clarence Loyd No. 1	E9	1949	— 2798	Quartzitic sandstone and shale	24
Suwannee	Sun, Earl Odum No. 1	F1	1947	— 2967	Black shale	24
Taylor	Humble, G. H. Hodges No. 1	F2	1948	— 5397	Diabase, probably a lava flow, under Triassic? or Jurassic? clastics	24
Dixie	Sun, P. C. Crapps "A", No. 1	F3	1949	— 4975	Sandstone and shale	24
Dixie	Sun, Hazel Langston No. 1	F4	1946	— 3612	Quartzitic sandstone and shale	24
Gilchrist	Sun, Williams Bros. No. 1	F5	1948	— 3271	Quartzitic sandstone and shale	24
Gilchrist	Sun, Alto Adams No. 1	F6	1946	— 3495	Quartzitic sandstone and shale	24
Alachua	Tidewater, R. H. Cato No. 1	F7	1947	— 3023	Quartzitic sandstone and shale	24
Alachua	Tidewater, Josie Parker No. 1	F8	1947	— 3002	Quartzitic sandstone and shale	24
Bradford	Tidewater, M. F. Wiggins No. 1	F9	1947	— 2999	Quartzitic sandstone and shale	24
Clay	Humble, Foremost Prop. Corp. No. 1	G1	1947	— 3610	Quartzitic sandstone	24
Alachua	Tidewater, J. A. Phifer No. 1	G2	1947	— 3085	Quartzitic sandstone and shale	24
Putnam	Sun Oil and Seaboard Oil, Q. I. Roberts No. 1A	G3	1947	— 3114	Quartzitic sandstone	24
Dixie	Stanolind and Sun, Perpetual Forest, Inc. No. 1	G4	1946	— 5195	Quartzitic sandstone	24
Levy	Coastal Pet. Co., J. B. and J. T. Ragland No. 1	G5	1947	— 5796	Black shale	24
Levy	Sun, J. T. Goethe No. 1	G6	1946	— 3926	Quartzitic sandstone	24
Levy	Humble, C. E. Robinson No. 1	G7	1949	— 4319	4319–4344, decomposed igneous rock under Lower Cretaceous sandstone 4344–4377, basalt; overlies 6 in. of altered black shale and quartzitic sandstone	24
Marion	Ocala Oil, Clark–Ray–Johnson No. 1	G8	1928	— 4200?	Quartzitic sandstone	24
Marion	J. S. Cosden, W. L. Lawson No. 1	G9	1928	— 3465	Quartzitic sandstone	24
Marion	Sun, H. T. Parker No. 1	H1	1949	— 3600	Quartzitic sandstone	24
Marion	Sun, H. C. Camp No. 1	H2	1947	— 4541	Volcanic agglomerate or tuff of rhyolitic composition	24
Putnam	Sun, H. E. Westbury *et al.*, No. 1	H3	1949	— 3841	Volcanic ash and tuff	24
Flager	Humble, J. W. Campbell No. 1	H4	1947	— 4557	Tuff and volcanic agglomerate of rhyolitic composition	24
Volusia	Grace Drilling Co., Retail Lumber Co. No. 1	H5	1949	— 5359	Volcanic rock, no cores	24
Volusia	Sun, Powell Land Co. No. 1	H6	1946	— 5862	Hornblende diorite (F. F. Grout)	24

Table 3—continued

County	Well Description	No.	Date	Bedrock Elevation	Type of Rock	Ref.
Florida (contd.)						
Hernando	Sohio, Hernasco Corp. No. 1	H7	1946	− 7673	Quartzitic sandstone	24
Lake	Oil Dev. Co. of Florida, Mrs. E. B. Gholston No. 1	H8	1937	− 5983	"Granite" not studied petrographically	24
Osceola	Humble, N. Ray Carroll No. 1	H9	1946	− 7973	Altered and veined biotite granite (F. F. Grout)	24
Osceola	Humble, W. P. Hayman No. 1	J1	1946	− 8654	Rhyolite	24
Hillsborough	Humble, T. S. Jameson No. 1	J2	1946	− 9898	Rhyolite and volcanic agglomerate	24
Hardee	Humble, B. T. Keen No. 1	J3	1948	− 11745	Lava and pyroclastic rocks	24
Highlands	Humble, G. C. Carlton Estate No. 1	J4	1946	− 12504	Amygdaloidal basalt, rhyolite porphyry and related volcanic rocks	24
Palm Beach	Humble, Tucson Corp. No. 1	J5	1947		Bottomed in Jurassic? at − 13341	24
Collier	Humble, Lowndes-Treadwell No. 1	J6	1945		Bottomed in Lower Cretaceous at − 13284	24
Monroe	Peninsular Oil and Ref. Co., J. W. Cory No. 1	J7	1939		Bottomed in Lower Cretaceous at − 9992	24
Dade	Humble, State of Fla. No. 1	J8	1945		Bottomed in Lower Cretaceous at − 11779	24
Collier	Humble, Gulf Coast Realties Co. No. 2	J9	1944		Bottomed in Lower Cretaceous (Trinity) at − 13478	24
Monroe	Gulf, State of Fla. No. 1	K0	1947		Bottomed in Jurassic? at − 15432	24
Alabama						
Houston	Johnston & Hawkins Co., Willis No. 1	K1	1940	− 7416	Ordovician? dolomite	24
Escambia	Humble, M. E. Skinner No. 1	K2	1944		Bottomed in Lower Cretaceous or older Mesozoic at − 10831	24
Crenshaw	Nelson Expl. Co., Smith Lumber Co. No. 1	K3	1948	− 10434	Triassic?	24
Barbour	W. B. Hinton, J. S. Creel No. 1	K4	1939	− 4838	Diabase sills or dikes in clastic rocks of Triassic? age; not studied petrographically	24
Barbour	H. A. Stebinger, A. S. Robertson No. 1	K5	1939	− 4661	Diabase sills or dikes in clastic rocks of Triassic? age (Chas. Milton)	24
Bullock	Capital Oil and Gas Co., Fred Pickett No. 1	K6	1945	− 2065	Metamorphic rock, probably gneiss, no cores	24

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Bullock	Capital Oil and Gas Co., Mrs. E. B. Gholston No. 1	K7	1945	— 1398	Diorite gneiss (Chas. Milton, U.S.G.S.)	24
Montgomery	Montgomery Oil Co., Snowdoun No. 1	K8	1923	— 1673	"Crystalline rock"	24
Wilcox	Seaboard Oil Co., S. M. McConnico No. 1	K9	1945	— 5332	Granite gneiss (Chas. Milton, U.S.G.S.)	24
Washington	Humble, J. R. Williams No. 1	L1	1949		Bottomed in Jurassic at — 15395	24
Clarke	Union Prod. Co., M. M. Waite No. 1	L2	1941		Bottomed in Jurassic at — 12361	24
Marengo	E. C. Johnston, H. D. Peteet No. 1	L3	1944	— 3628	Hard gray limestone; Black River or Trenton	24
Greene	Johnson and Hawkins Co., Willis No. 1	L4	1940	— 2220	Dolomite, Ordovician?	24
Pickens	C. H. Murphy, Jr., Oden–Eaton No. 1	L5	1946	— 635	Pennsylvanian, chiefly clastics	24
Lamar	DeSoto Oil and Gas Co., Gardner No. 1	L6	1936	— 204	Pennsylvanian to Silurian	24
Lamar	Stanolind, Jack Woods No. 1	L7	1944	92	Pennsylvanian–Mississippian	24
Lamar	Briggs and Knapp, Wefel No. 1	L8	1930	385	Mississippian limestone	24

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A great many of the fossils, which include ostracods, conodonts, brachiopods, cephalopods, gastropods, pelycepods, graptolites, trilobites, eurypterids, crinoid stems, and worm tubes represent new species. The sediments are chiefly quartzitic sandstones and dark shales and for the most part are horizontally bedded and unmetamorphosed. One well showed dips of 20 to 25° and the recrystallization of quartz grains in a few cores has been interpreted by some as evidence of incipient metamorphism (APPLIN, 1951). The thickness of the Paleozoic section has been estimated as 6000 feet or greater (BRIDGE and BERDAN, 1950). The volcanics are rhyolitic and basaltic tuffs, flows and agglomerates overlain by Lower Cretaceous in some places and by unfossiliferous Paleozoics in one well in

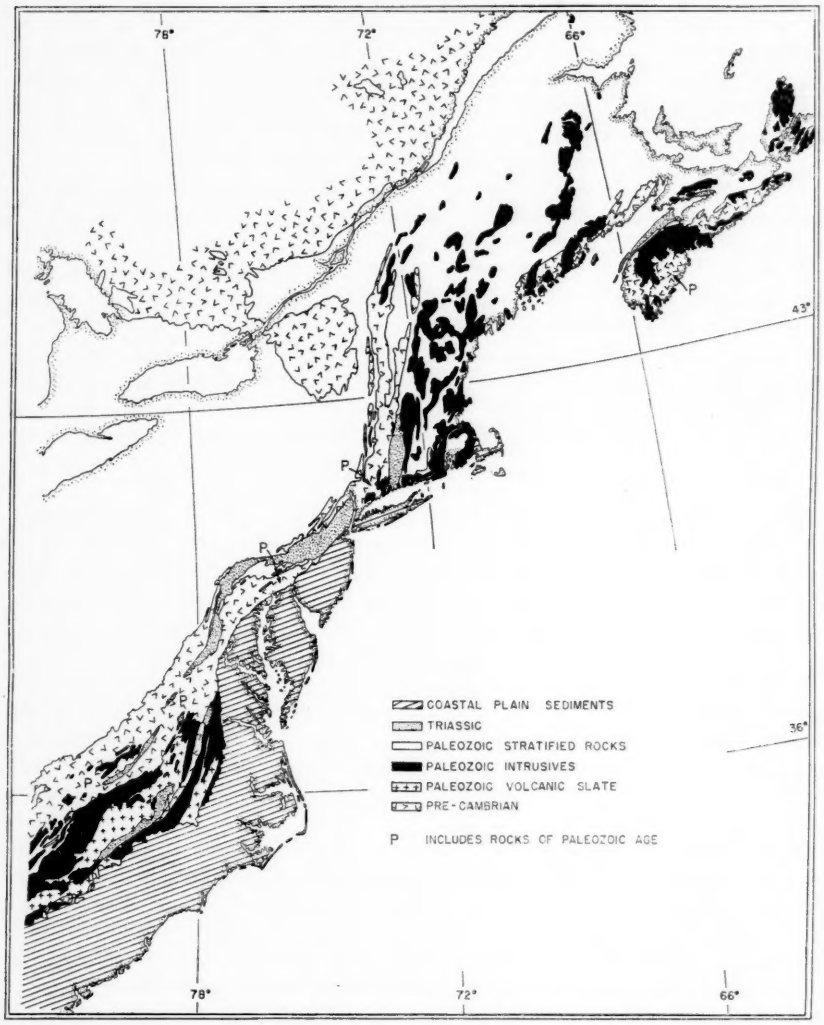

Fig. 22. Geology of eastern North America (after Geologic Map of North America, 1932).

central Florida. They have been tentatively classified as early Paleozoic or possibly Pre-Cambrian.

Rocks similar to these are found in North Carolina, Georgia, and Virginia. They are on the south-east edge of the Piedmont province and are shown on Fig. 22 as "Paleozoic volcanic slates" after the terminology of the Geologic Map of North America (1946). They are represented as Pre-Cambrian (Algonkian?) on the Geologic Map of the United States (1933). These rocks (Virgilina volcanic series in Virginia, Little River Series in Georgia, and the Volcanic Slate Belt of North Carolina) consist of flows, breccias, and bedded tuffs of volcanic origin, with some interbedded slates and sandstones (KING, 1950, p. 656). The structure has been described by LANEY (1910, p. 66):

"As distance from the (fault) contact with the igneous rocks increases, the folding becomes less and less prominent, and along the extreme eastern edge of the area studied, the rocks are massive and present little or no effects of dynamic metamorphism. A traverse of between 20 and 30 miles (eastward) beyond the confines of the area mapped, showed that the intensity of the folding continued to decrease. In many places the strata were practically horizontal."

The concept of a two-sided system, as suggested by KING (1950, p. 639), with metamorphism decreasing in both directions from a centre (Fig. 23), appears to be real in the south-eastern states.

If we assume that conditions to the north are similar, then it would appear that the major cause of the decrease in velocity is indeed a change in character from crystallines to sediments, pyroclastics and volcanic flows. Furthermore, if the age relations hold, then these formations do not in their entirety represent material derived from the lands created by the Ordovician orogenies but are, at least in part, pre-Taconic material on the seaward side of the eugeosynclinal belt which was not subjected to the metamorphic processes of the belt proper.

Ocean Crust and Mantle

Direct correlation of the velocities found in the ocean crust and mantle with lithology is not possible. Indirect evidence has been used to identify them, however, and the arguments have been cited by BULLARD (1954b, pp. 404–405) and HESS (1954, pp. 341–342). An oceanic crust of basaltic composition is compatible with gravity and density figures; oceanic islands give no evidence of another material, and the measured seismic velocities are in the right range for this material. Peridotite, the presumed major constituent of the mantle, is petrologically likely, is composed of common elements and has the correct seismic velocity. Its density is of the right order and it has a low alkali and uranium content. HESS (1954) has suggested that reported xenoliths of peridotite in basaltic volcanic rocks represent mantle material which has been brought to the surface.

ROBERTSON *et al.* (1957, pp. 133–137) have presented evidence that the Mohorovicic discontinuity may represent a phase change rather than a change in chemical composition. Their study of the albite–jadeite–nepheline system shows that jadeite, with a density of about 3·3, can form from a nepheline–albite mixture (density about 2·6) at temperatures and pressures which may be expected to exist in the vicinity of the Mohorovicic discontinuity under the continents. It is more difficult to account for the Mohorovicic discontinuity under the oceans in terms of this phase change since the albite–nepheline combination

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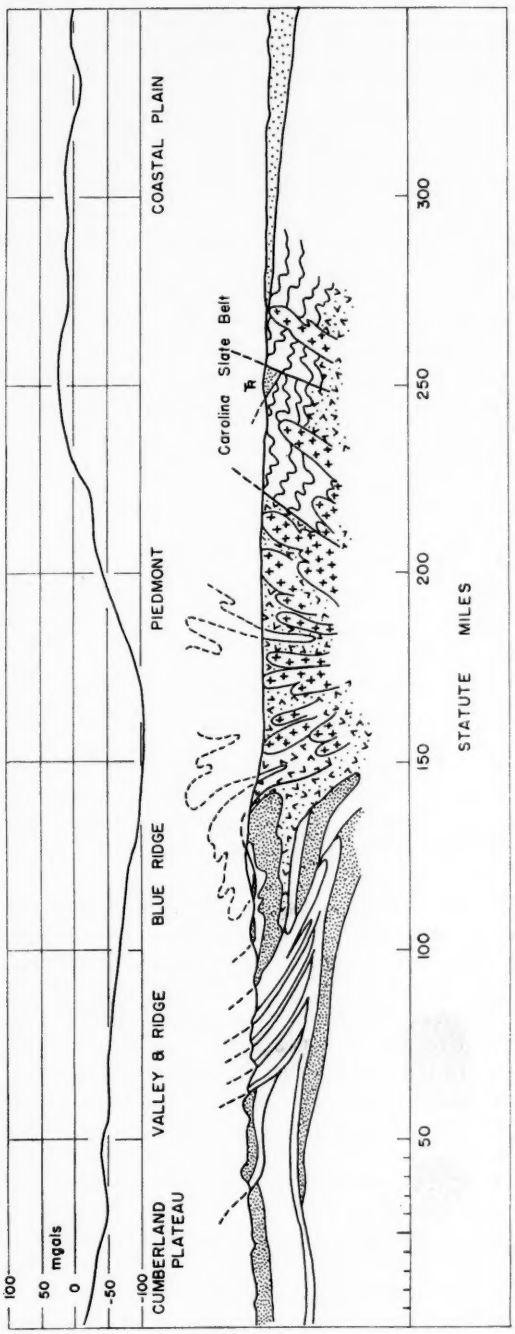

Fig. 23. Diagrammatic cross-section of Southern Appalachians (after KING, 1950; gravity after WOOLLARD).

appears to be stable to depths of about 38 km. In view of the uncertain thermal conditions in the ocean regions and allowing for additional components in the silicate system, this result should not be taken as final. Certainly the hypothesis should be considered as a possibility pending additional data.

KATZ and EWING (1956, p. 489) analysed the distribution of seismic velocities from stations at depths over 1000 fathoms without regard to areal distribution. They found well defined groups centered about 2·4, 4·4, 5·5, 6·3, 6·8 and 8·1 km/sec.

The 8·1 km/sec layer represents the mantle as we have defined it and the oceanic crust appears to fall in both the 6·3 and the 6·8 km/sec groups depending on location. Near the continents the velocities in the oceanic crust increase to an average velocity of about 7·0 km/sec with one as high as 7·59 km/sec. It becomes difficult to correlate between profiles when the velocities approach those in the mantle. This is best illustrated in the Newfoundland section (Fig. 35, modified after BENTLEY and WORZEL, 1956). Here we find the following distribution of velocities:

Profile	10	9	8	7	6
	1·96	1·84	1·79	1·78	1·79
	2·60	2·36	2·31	2·63	2·66, 2·55
	4·28	3·68	4·14	3·84	3·93
	5·45	5·97	5·87	5·78	—
			7·24	7·59	6·70
					7·75

Profile 6 approaches the configuration usually found in ocean basins but has a low velocity in the mantle. The profiles to the north, toward Newfoundland, show only a single layer of velocity greater than 6·0 km/sec and the velocity in this layer is intermediate between those usually found in the oceanic crust and the mantle.

J. EWING and M. EWING (1957) reports similar structure on the Mid-Atlantic Ridge where a crustal velocity of 7·2–7·6 km/sec was found and no discontinuity was observed below this layer even on a very long profile. OFFICER *et al.* (1952, p. 800) found the same type of structure near Bermuda where a single layer with a velocity of about 7·2 km/sec was measured. They suggested two possibilities to explain this: either it reflects intrusive activity associated with the Bermuda volcanics and mixing of the two layers or it represents a primary feature of the basement structure which has served to localize the Bermuda volcanoes. If it is due to mixing, then the mixing must be thorough enough that the individual velocity measurements fall near the average. This precludes movement of mantle material upwards along a single fault plane and implies either thorough assimilation or many closely spaced intrusions.

Ultrabasic intrusions in orogenic belts show a character of the latter type (TALIAFERO, 1943; PRATT and LEWIS, 1905; BENSON, 1926), but they appear at the surface to be much too localized to account for the velocity change. This objection might be overcome if we allow that the ultrabasics only approach

the surface where the orogenic forces are of maximum strength and that they are present but deeper on each side of the centre.

HESS (1955, pp. 391–408) has suggested that serpentinization of the olivine of the mantle may have a bearing on orogenic and epeirogenic processes. Such serpentinization would cause a decrease in density within the upper part of the mantle accompanied by a probable decrease in the velocity of compressional waves. This process, like the previous one, could increase the total thickness of a layer having intermediate velocity and, as outlined by Hess, might occur over a sufficiently large area to explain the observed velocities.

The phase-change suggestion of ROBERTSON *et al.* (*op. cit.*) would do equally well. Velocities intermediate between those of the oceanic crust and the mantle might be expected in regions where the thermal conditions are variable or only partial equilibrium of the reactions has been attained. Changes in both mantle and oceanic crustal velocities may be accounted for by this hypothesis while that of Hess considers only the mantle.

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An alternative explanation is possible if the thickness of the oceanic crustal layer is not considerably greater than the wavelength of the observed sound arrivals. PRESS *et al.* (*op. cit.*, pp. 388–401) have demonstrated with model experiments that a thin layer at depth will give anomalous velocities. Their study of a three-layer case with a thin intermediate layer showed no velocity appropriate for the intermediate layer. The first arrivals indicated a break from the velocity in the upper layer to a velocity intermediate between those in the lower two. If it can be shown that the thickness to wavelength ratio off the shelf is similar to that of the model experiment, this explanation may be the correct one. Unfortunately, it would be difficult to determine this by standard refraction methods. We may, however, examine the gravity data for an independent test of such an explanation.

OTHER GEOPHYSICAL DATA

Gravity Measurements

The new seismic information makes it possible to interpret in greater detail the gravity data across the continental margin (WORZEL and SHURBET, 1955, pp. 458–469). Before making any calculations, however, let us examine the premises upon which the interpretations will be based.

Interpretation of large scale gravity features may be based on density variations within the layers of the earth on one extreme, on variations in thickness of layers of essentially constant density on the other extreme, or on some combination of these two factors. If isostatic equilibrium is assumed and the first of these possibilities is the most applicable, there should be no systematic relation between crustal thickness and elevation above and below sea level, while if the second is more suitable, such a relationship should be observed. If a combination of these two factors is the case, the degree of correlation between thickness and elevation will depend on their relative importance.

Sufficient seismic information is available that a plot may be made of crustal thickness vs. elevation. If sub-aerial and submarine values are to be compared, however, it is necessary to make adjustments for the water in the latter regions. This can be done either by compressing the water column into an equivalent thickness of material with density of the crustal rocks and reducing the water

depth and increasing the crustal thickness by this quantity or by removing the water and shifting the crust–mantle boundary an amount sufficient to account for its gravitational effect. Although the latter method results in negative crustal thicknesses for water depths greater than about 4 km, it was used since it has the effect of spreading the data.

Figure 24 shows the results of plotting adjusted crustal thickness against elevation. It should be noted that no allowance has been made for lack of isostatic equilibrium. For most of the oceanic stations, excluding the island arc areas, this effect should be small, but it may be significant for the land stations.

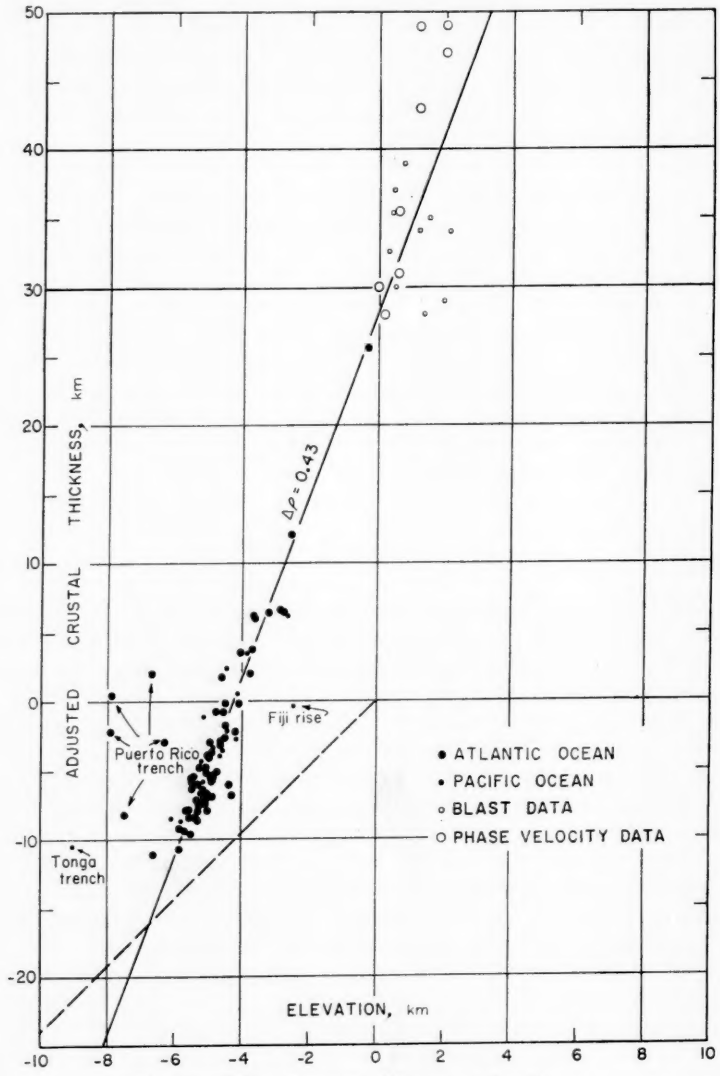

Fig. 24. Adjusted crustal thickness vs. elevation.

The results indicate that there is a relationship between crustal thickness and elevation and that calculations based on a constant crust–mantle density ratio will yield a rough first approximation of the structure. Although there is considerable scatter of the continental values, the oceanic ones, with the exception of those in the vicinity of trenches and one from the Fiji Rise, are quite systematic. The line through these data represents a density difference between the crust and the mantle of 0·43 g/cm³, the value determined by WORZEL and SHURBET (1955, p. 92).

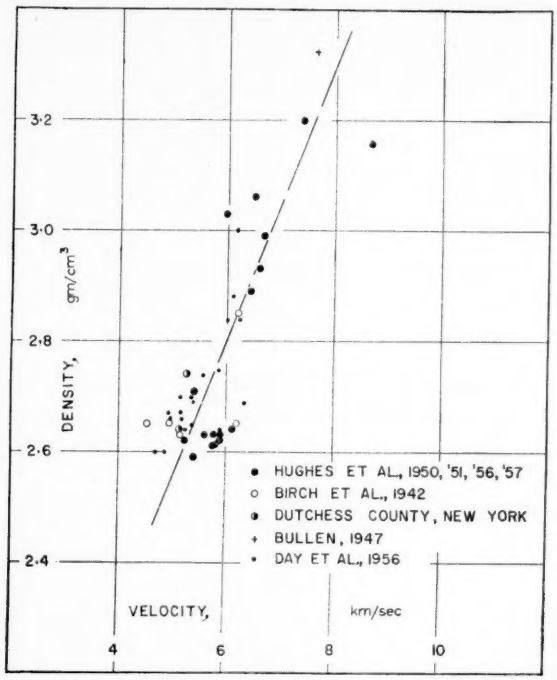

Fig. 25. Velocity–density relationships in igneous and metamorphic rocks.

The dashed line in the lower part of Fig. 24 indicates the adjustments in crustal thickness made for different depths of water. If the crust–mantle density difference is 0·43 g/cm³, then, with isostatic equilibrium, the crustal thickness must reach zero where the dashed line crosses the solid one. At greater depths isostatic equilibrium is not possible unless the mantle density is increased. Thus the deep trenches must be out of equilibrium unless the mantle densities in these regions are of the order of 3·4 g/cm³ or more.

The interpretations may be improved if we can relate density to some known parameter of the earth. The only such quantities which are of use at the present time are seismic velocities. The available data relating compressional wave velocity to density of igneous and metamorphic rocks are shown in Fig. 25. It can be seen that, for average mantle velocities of about 8 km/sec and average crustal velocities of 6 + km/sec that the density difference chosen by Worzel and Shurbet is a reasonable one and that the absolute values of 2·84 g/cm³ for the

crust and 3·27 g/cm³ for the mantle do not conflict with these data. It is probable that the compensating effects of temperature and pressure will prevent any large variations from these values in the depth range under consideration (GUTENBERG, 1955, pp. 43–50).

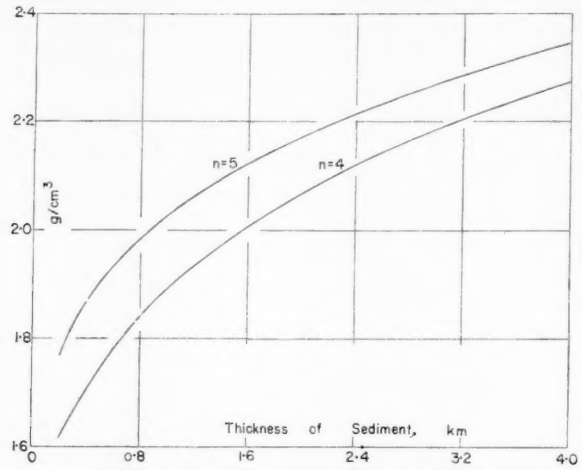

Fig. 26. Mean density as a function of thickness in shallow water sediments (after NAFE and DRAKE, 1957).

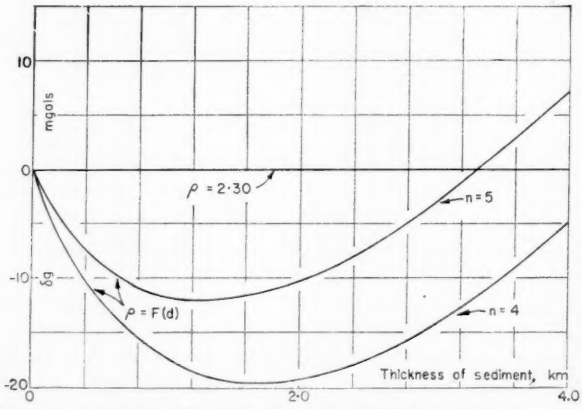

Fig. 27. Differences in gravitational effect between thicknesses of sediment of constant density and equal thicknesses for which density is a function of the thickness.

The variation of density with velocity in marine sediments has been studied by NAFE and DRAKE (1957). For the sediments of the continental shelf north of Cape Hatteras the mean density of the sedimentary column will vary with the thickness of the column approximately as the curves of Fig. 26. The $n = 5$ curve has been found empirically to be the best approximation for sands and shales while the $n = 4$ curve is more appropriate for limestones. The differences in gravitational attraction of infinite sheets of sediment with these density

gradients and that with a constant density of 2·30 g/cm³ are shown in Fig. 27. In most of the area under study the sediment thicknesses are such that differences of only a few milligals may be expected. Use of the density gradient will not change the final picture appreciably.

The gravity section from Portland, Maine, to sea has been recalculated on the basis of the above assumptions. Four cases have been examined using the densities outlined in Fig. 28. For the first two cases the density of all the crustal rocks was taken to be 2·84 g/cm³, following Worzel and Shurbet, while the crust was divided into two parts in the latter cases.

It can be seen (Fig. 28) that there are no major differences between cases I and II. In both cases the sharp flexure in the Mohorovicic discontinuity occurs at approximately the same place and is of the same order of magnitude and there is an upward bulge of the mantle on the continental side of the flexure. Since the differences are small, it is reasonable to use the density 2·30 g/cm³ for the sediments in the calculations.

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In case III the crust was divided into two parts, continental and oceanic. The boundary between these two layers was determined seismically where marked by a solid line on the section of Fig. 28 and was inferred where dashed. The crustal densities were chosen to conform with the measured velocities (Fig. 25) and to make the mean crustal density approximate 2·84 g/cm³. The layering was continued under the continent to avoid edge effects although there is some question whether discrete layering exists in the continental crust. The choice of densities under the continent and the relative thicknesses of the layers are in agreement with those implied from studies of higher modes of earthquake surface waves (Oliver and Ewing, 1957).

The principal differences between case III and the first two are the elimination of the upward bulge of the mantle under the continental shelf, and a somewhat thinner oceanic crust on the ocean side of the flexure in the Mohorovicic discontinuity. The thickness here is such that, for seismic frequencies, the thickness–wavelength ratio is similar to that of Press *et al.* (1954) and the measured velocities may not be indicative of the materials present at depth.

In case III the choice of densities and configurations of the layers above the mantle is offered as the best which can be made from the available data. The mantle velocity, and its density, are unknown except at the extreme ends of the section. There are indications that the mantle velocities are less than 8 km/sec near the margin, which would imply a density of less than 3·27 g/cm³. If the mantle density were reduced by more than a few hundredths of a g/cm³, however, the calculated oceanic crustal layer thickness would become negative. Case IV demonstrates the effect of increasing the mantle density by 0·14 g/cm³. A reduction of the mantle density by the same amount would have a similar effect in the opposite direction.

An indication of the degree of isostatic balance may be obtained by comparing the masses of vertical columns along the section. This has been done for cases I–III and the results are plotted in Fig. 28 in terms of mean density to 35 km. Cases I and II both show sharp variations near the edge of the shelf while case III varies smoothly across it. These variations are most likely due to the density distribution required to match the observed anomaly curve rather than to a real isostatic unbalance and the smoothness of the curve of case III might be taken as an additional argument in its favour.

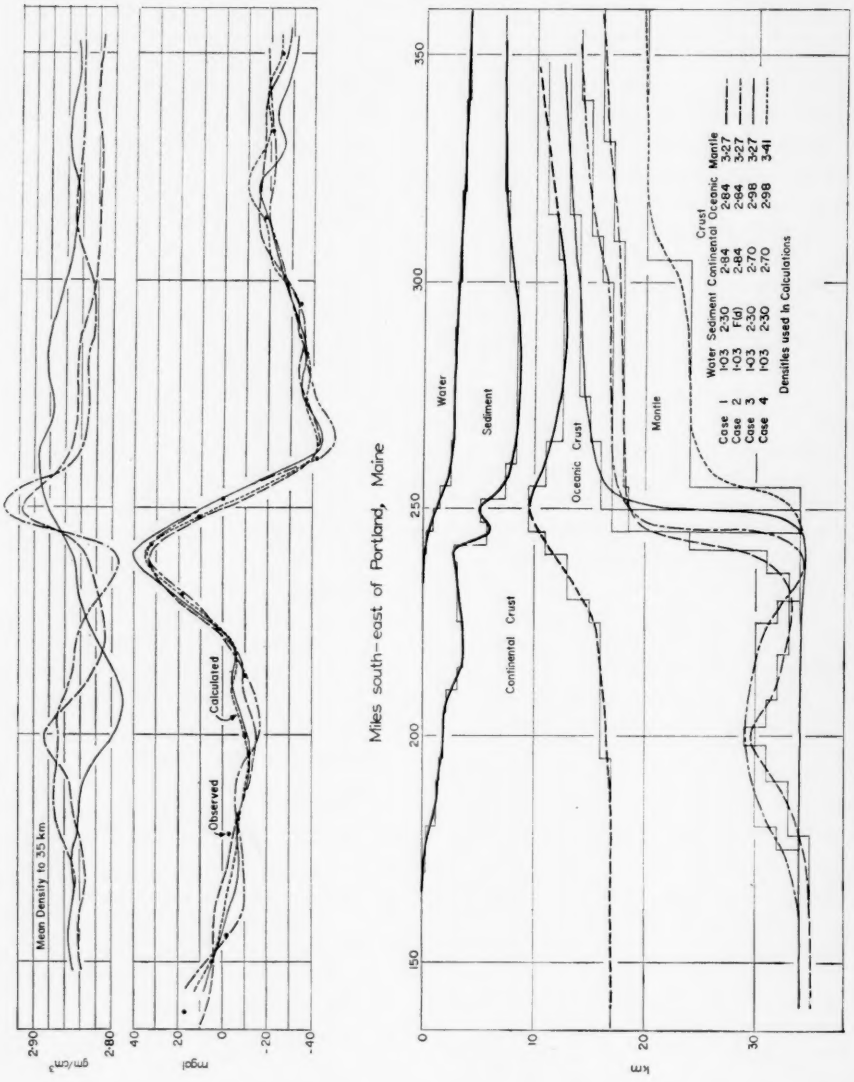

Fig. 28. Gravity and structure sections, Portland, Maine, line.

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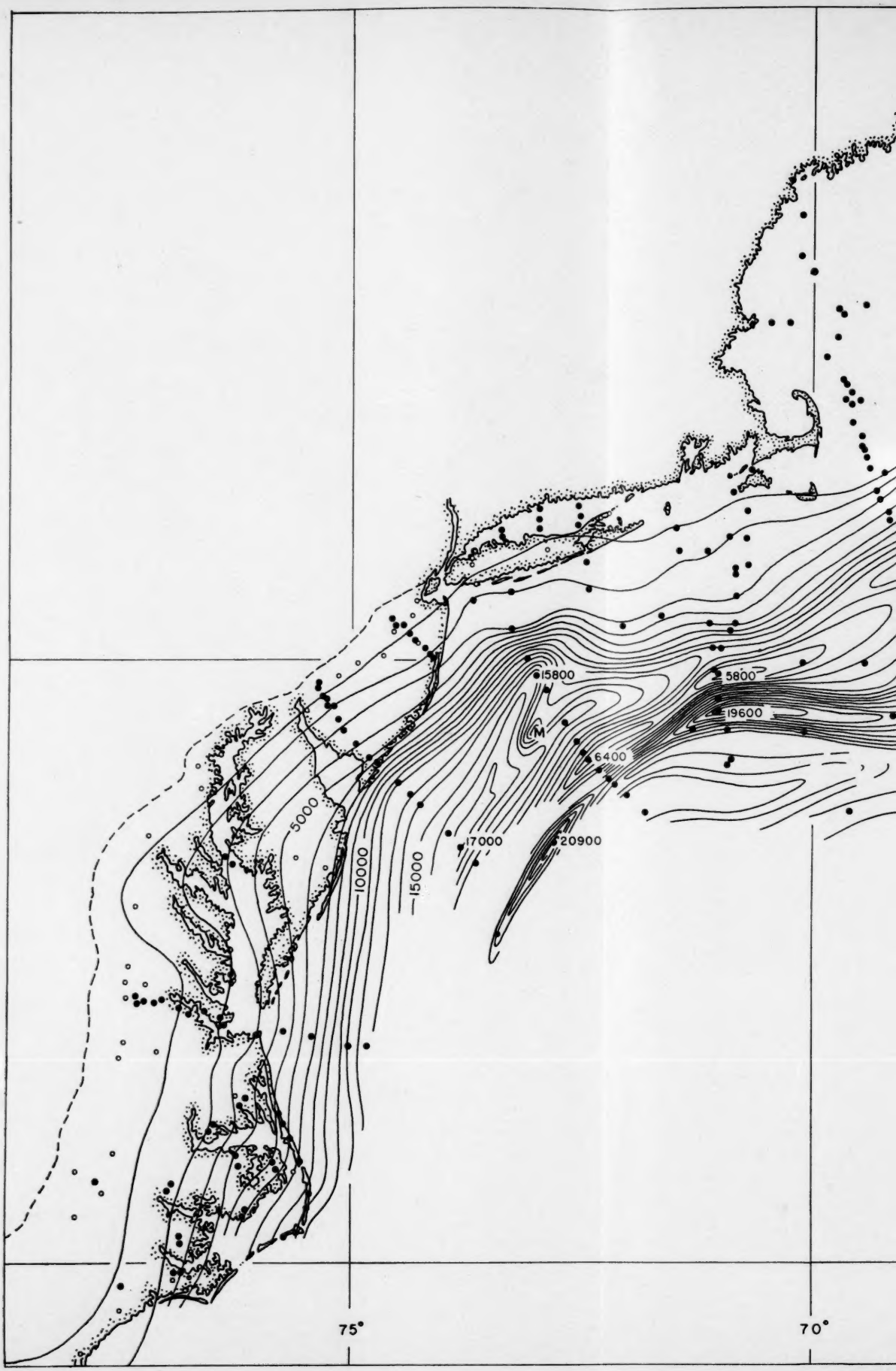
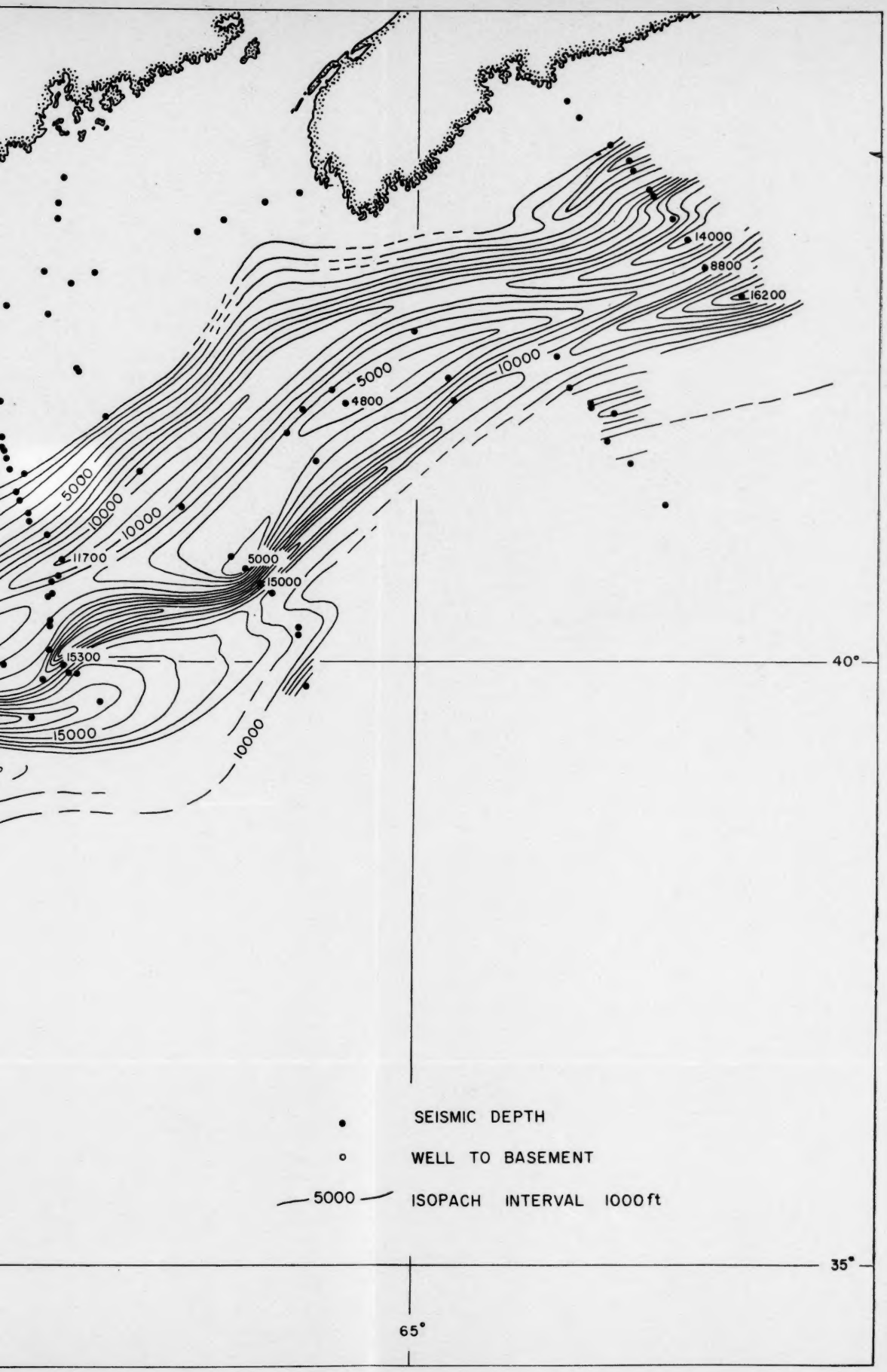


Fig. 29. Isopach map of to



of total sediment thickness.

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The gravity measurements on the Woods Hole and the New York lines have been re-examined on the basis of the new seismic information and calculations made using the density assumptions of case I. There are insufficient data on the configuration of the boundary between continental and oceanic crust to permit application of case III densities. Although the distribution of sediments and the shape of the anomaly curves for these two sections are quite different from those of the Portland line, the computed configuration of the Mohorovicic discontinuity for each of these sections is identical in magnitude and shape with case I of the latter. This suggests that there is a uniformity of deep structure along the margin at least as far south as Cape Hatteras and that variations in the anomaly curves in this region are due to variations in sediment thickness.

Magnetic Data

A considerable body of magnetic data has been collected in this area using an MAD flux-gate magnetometer modified for marine use (HEEZEN *et al.*, 1953). Qualitative examination of the data reveals several interesting anomalies.

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The major magnetic anomaly associated with the continental margin is a positive one of several hundred gammas amplitude which has been observed at the edge of the shelf on numerous crossings (MILLER and EWING, 1956, p. 412). The anomaly may be associated with the basement ridge shown on the sections of Fig. 35 (KELLER *et al.*, 1954, pp. 570–571). South of Cape Hatteras it loses its distinctiveness and a series of three or four linear anomalies paralleling the coast extends into the Blake Plateau area (J. Hirshman, personal communication). The amplitude of the anomaly is such that the basement might be expected to consist in part of volcanic material. This is in agreement with the projected basement geology.

A number of circular anomalies have been observed, all except one being located off the edge of the shelf. These are, in most cases, associated with seamounts of volcanic origin. The one on the shelf is located about 40 miles southeast of Barnegat Lightship in 25 fathoms of water and is marked "M" on the isopach map (Fig. 29). According to E. T. Miller (personal communication) the influencing body must rise above the basement surface if it is to have a reasonable susceptibility and probably represents a buried volcanic centre. The sedimentary velocities in the vicinity of this feature are similar to those at some distance. This might be taken as an indication that the volcanic centre was emplaced prior to the sedimentation. No signs of volcanic activity have been noted in the sediments of the adjacent shelves.

The age of the seamounts off the edge of the shelf is quite conjectural. A core taken on top of one south of Georges Bank penetrated sediments entirely of Pleistocene age. There was no trace of volcanic activity (SHURBET and WORZEL, 1955, p. 777). Ericson has dated Caryn Peak (37N, 68W) as Upper Cretaceous on the basis of alteration of fossils (MILLER and EWING, 1956, p. 424), but it may be unrelated to those nearer to the continental margin. Little volcanic ash has been found in ocean cores off the East Coast although some, tentatively dated as Eocene to Oligocene, has been recovered off Bermuda (ERICSON *et al.*, 1952). If the volcanism were submarine, ash might well be localized. Furthermore, since the continental slope and rise are subject to slumping and turbidity current action, thin ash beds might be destroyed. It is possible that there was Cenozoic volcanism in the area but it seems more likely that it was Mesozoic in age.

STRUCTURE SECTIONS AND ISOPACHS

The depth and thickness data are presented in the form of structure sections (Fig. 35) and as an isopach map of total sediment thickness (Fig. 29). The sedimentary nomenclature is that outlined previously and may have no stratigraphic significance.

All of the structure sections show the same general features. Starting from the shore, the coastal plain sediments thicken to form a trough from 3 to 6 km in depth. This trough is bounded, near the edge of the continental shelf by a ridge in the basement which reduces the sediment thickness to between 1·5 to 2·5 km. On the ocean side of this is another trough containing up to 8 km of sediment. The sediment thins seaward from this trough until it reaches the average thickness of 1 km found in the ocean basin. The development of these features varies from section to section but the overall relationships are the same. The isopachs of Fig. 29 show these features in a very striking manner. These were not extended to the Newfoundland section due to lack of data between this section and that off Halifax.

Beneath the sediments the basement rocks thin and eventually pinch out under the ocean basin. There appears to be considerable variation in extent. Under the Newfoundland profile these rocks extend some 200 miles beyond the edge of the shelf, while they are limited to about 50 miles under the Matinicus–Georges Bank section. Near centres of submarine volcanism the picture becomes complicated since the volcanics have velocities in the same range as those of the basement rocks off the edge of the shelf.

There is an indication that the oceanic crustal layer rises somewhat near the edge of the continent before dipping down and possibly merging with the continental material. This rise is shown best on the Halifax and Portland sections and the four profiles between the Portland and Woods Hole sections and is suggested on some of the other sections. A similar rise has been observed off the coast of Brazil (WARREN and EWING, 1958) and Argentina (Ludwig, personal communication). In general, there is a thinning of the continental basement rocks where this rise occurs with the locus of the thinnest part near the axis of the outer trough mentioned earlier.

The depth to the Mohorovicic discontinuity was measured in a few places, but there are insufficient seismic data to allow conclusions to be drawn concerning its behaviour in the transition zone between oceanic and continental areas. It is well known that this discontinuity is at a depth of about 10 km beneath the surface of the oceans while under the continents it is three or four times as deep. The few measurements of its depth in this area show it to be dipping down toward the continent.

COMPARISON WITH APPALACHIAN SYSTEM

KAY (1951) divided the Appalachian orthogeosyncline into two major parts: an inner (shoreward) trough, termed a miogeosyncline, notable for its lack of volcanics, and an outer trough, the eugeosyncline, which is characterized by intermittent volcanic activity. The miogeosynclinal belt is typically folded and thrust-faulted while the major igneous and metamorphic activity took place in the eugeosynclinal belt. These two are separated by a geanticlinal barrier of

some description which serves to divide them sharply and to confine the effects of igneous activity principally to the outer, eugeosynclinal, trough.

The configuration of the region between the Fall line and the continental rise shows a great resemblance to that of the Appalachian system as it was presumed to be during the early stages of its development (Fig. 30). Here, as in the Appalachians, there are two troughs separated by a basement ridge. The outer trough may be compared with the Appalachian eugeosyncline, the inner with the miogeosyncline. It should be noted that the total thickness of material of sedimentary character in the outer trough may be greater than indicated on the isopachous sections of Fig. 30. The velocities in the continental crustal layer of this area are in the range typical of consolidated sediments and all or part of this layer might be included in the total sediment thickness.

Eugeosyncline

If we are to identify the outer trough with eugeosynclines, we should find signs of volcanic activity. While there is no activity at the present time, the magnetic results have revealed evidence of volcanism in the past. The geologic information from deep wells south of the area under consideration supports the notion that the basement rocks under the shelf, slope, and rise may be composed to a great extent of volcanic and pyroclastic material. The seismic velocities determined for these rocks are in good agreement with those of the volcanic slates of the Piedmont and volcanic rocks in the vicinity of Bermuda and the Mid-Atlantic Ridge. Furthermore, the velocity contours parallel the structure so well that it is logical to expect that conditions are similar along the strike of the system.

It would appear, then, that while the sediments lie on a volcanic terrain, there is a possibility of only limited volcanism, represented by the offshore seamounts, during Mesozoic or Tertiary time. Although this seems at first to conflict with the evidence from the Appalachian region, a closer examination of the data does not reveal any basic inconsistencies.

KAY (1951, pp. 49–57) gives examples of volcanics in the Appalachian eugeosyncline which range from Cambrian through Pennsylvanian in age. The dating is often doubtful and the age limits are wide in many cases. The Cambrian examples are particularly questionable. Kay reports that he is:

". . . not familiar with any volcanic rock within a section having Cambrian fossils above and below it. Some of the volcanics are Lower Cambrian because they are within sedimentary sequences conformably underlying fossiliferous Cambrian; others are considered to be Cambrian because they lie below Ordovician, and still others are correlated on stratigraphic and structural grounds." (1951, p. 52.)

Recent investigations in Cape Breton, Nova Scotia (HUTCHINSON, 1952) have revealed the presence of Middle Cambrian volcanics with Cambrian fossils both above and below, but this appears to be an isolated case. The dating is complicated by uncertain structural relationships, lack of fossils, prejudice, and disagreement as to the location of the base of the Cambrian. It would seem, nevertheless, that there are few volcanic outcrops of unquestionable Cambrian age, and that most of these are limited to the Lower Cambrian. This leaves a long period of time, at least a good fraction of the Cambrian for which little positive evidence of active volcanism has been obtained.

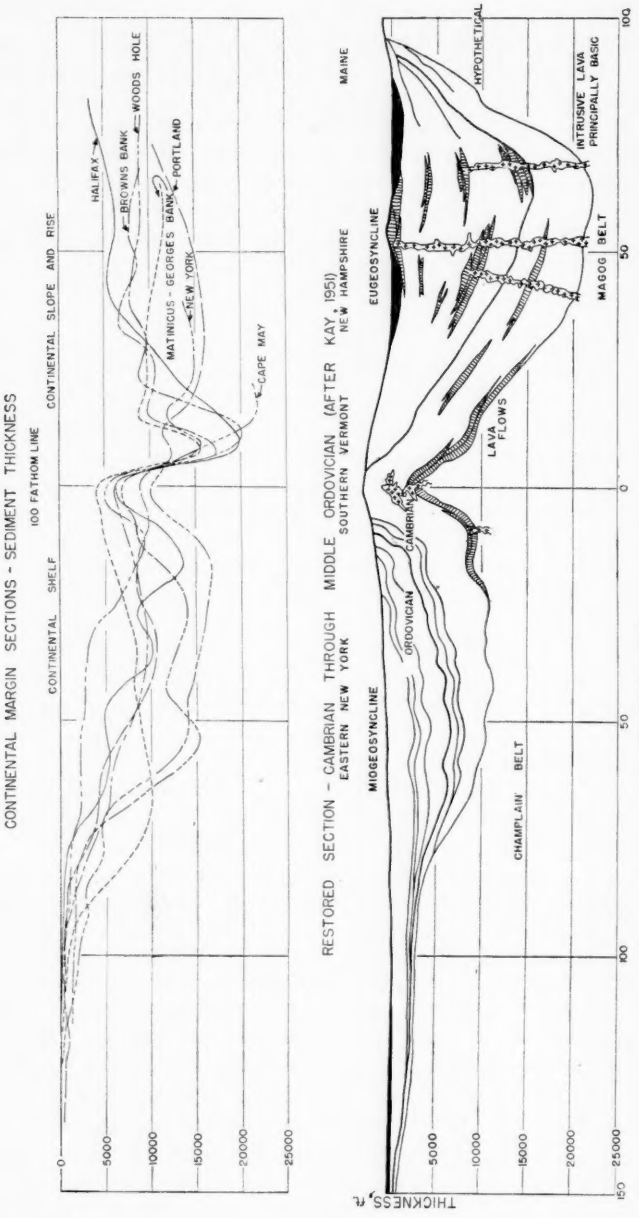

Fig. 30. Comparison between restored geosynclinal section (after KAY, 1951) and isopachous sections off the east coast of North America.

Activity was much more extensive in the Ordovician, particularly in the middle and upper parts (KAY, 1951, pp. 52–53), hence comparisons with the present continental margin must be restricted to the Cambrian or, perhaps, extended into the lower Ordovician. Within these limits, if we allow that some of the outcrops identified as Cambrian are, in reality, pre-Cambrian, there are no essential differences in quantity or distribution of volcanic activity between the two areas.

Placing the eugeosyncline in relatively deep water would serve to localize the effects of the volcanic activity. Although the miogeosyncline is immediately adjacent, it should receive no important amount of volcanic material if the activity is submarine. Furthermore, although the mechanism by which extrusive material is brought to the surface is poorly understood, it would logically seek the easiest path. The relatively abrupt transition zone between continent and ocean might be expected to be the region of maximum instability and hence favourable for igneous activity.

The association of greenstones and spilitic volcanics with the early geosynclinal sediments has been remarked by many observers (TURNER and VERHOOGEN, 1951, pp. 201–212; DEWEY and FLETT, 1911, pp. 202–209; BLOOMER and WERNER, 1955, pp. 589–594; KNOPF, 1948, pp. 649–670; PARK, 1946, pp. 305–323; TALIAFERO, 1943, pp. 144–147; and others) and the problems connected with the origin of spilites have been outlined by GILLULY (1935, pp. 234–244). The association of these rocks with radiolarian cherts and the frequently found pillow structure of the volcanics support a submarine origin. While the secondary origin of the albite is not universally accepted, the suggested deep-water environment of emplacement might favour such a secondary origin.

If eugeosynclinal sediments of older systems were deposited in an environment similar to that of the outer trough, there should be evidence of this in the geologic record. Most of the information regarding the sedimentary processes which affect the continental slope and rise is of recent origin. The high degree of metamorphism and the confusion caused by emplacement of igneous bodies and volcanics have made it difficult to determine the sedimentary character in eugeosynclinal belts except in more or less limited areas. The problem is made more complex in the Piedmont area of the southern Appalachians by the deep weathering.

In spite of the difficulties, it is becoming apparent that sediments from this type of environment are more widespread than has been assumed in the past. BAILEY (1930, pp. 86–88) recognized the deep water character of graywackes although it was not clear at that time how the sands were emplaced. PETTIJOHN (1943, pp. 925–972) noted that crossbedding and ripple marks were scarce in Archean graywackes and that graded bedding was common. A mechanism for the formation of these features was presented by KUENEN and MIGLIORINI (1950, pp. 91–127) in the form of turbidity currents. The characteristics to be expected of sediments subjected to these currents were outlined in some detail by KUENEN (1953, pp. 1045–1047). Studies of modern sediments in submarine cores from the continental slope and rise have shown that the graded bedding commonly found may be attributed to the transporting characteristics and the intermittent nature of turbidity currents (ERICSON *et al.*, 1951, 1952; HEEZEN and EWING, 1952; EWING and HEEZEN, 1955; HEEZEN *et al.*, 1954). In addition it has been shown that coarse, angular clastics can be deposited near the base

of the continental slope, that shallow water fauna can be carried down without apparent damage, that breccias of soft clay and limestone can form, and that such minerals as glauconite, calcite, and feldspars may be present.

PETTIJOHN (1950) attributed the apparent lack of modern graywackes to the fact that they are being formed by turbidity currents in deep water and pointed out that the features attributed to turbidity current deposition were those found in graywackes from Archean to Tertiary in age. Similar features have been found by others. BAILEY (1936) noted the occurrence of graded bedding of many ages:

". . . . the younger Dalradian (probably late Pre-Cambrian), Cambrian, Ordovician, and Silurian of Scotland, Ireland, and Wales within the compass of the Caldonian geosyncline . . . it characterizes some of the Amorican geosyncline of the Devon Peninsula and . . . the Tertiary Flysch of the Alpine geosyncline."

The absence of ripple marks and cross bedding in the Franciscan (Jurassic) of California and the even bedding have been noted by DAVIS (1918, pp. 38–39). Sands are interbedded with radiolarian cherts, foraminiferal limestones, and shales (TALIAFERO, 1943, p. 132). KUENEN and MIGLIORINI (1950, pp. 109–113) believe that the Macigno and the brecciolas of the northern Apennines have been deposited by turbidity currents, the differences between the two being attributed to higher velocity currents in the latter case. KUENEN gives further examples from Wales and from California (1953, pp. 1060–1065), and from Germany (1956, pp. 649–671).

RICH (1950, pp. 717–741) has examined the Silurian rocks of Wales and finds evidence that they were deposited in a continental slope environment. The deposits are marked by a scarcity of fossils, evenness of bedding, flow markings, few ripple marks and only small-scale, vague cross-bedding. RICH (*op. cit.*, p. 739) has found that, within his experience, it is:

". . . difficult to find rocks consisting of thin evenly bedded alternations of siltstone and shale (or their calcareous equivalents) which do not show these flowage phenomena."

JONES (1955, p. 330) describes the Aberystwyth grit group near Cwmystwyth in Wales as a 4000 ft series of coarse and fine sediments alternating every foot or two. He further notes the presence of a slump structures of many types in the rocks of this area. In an earlier paper (1937) he mentions heavy shelled shelf fossils carried down by slumping.

Pettijohn (1949, pp. 254–255) notes that graywackes of his definition are the most typical sediments of some orogenic belts and do not occur in any important manner outside of this environment.

". . . The early pre-Cambrian of Ontario (excluding the Grenville), commonly called Timiskaming, is 90 per cent graywacke. Such apparently is also true of the Pre-Karelidic deposits of Finland. . . . Some parts of the Huronian also are marked by thick graywackes and associated slates. . . . The graywacke suite is typical of the Lower Paleozoic of Great Britain in the Caledonian geosyncline of Wales, the Lake District of England, and the Southern Highlands of Scotland, where it is associated with pillow lavas and cherts. Graywackes occur in the Devonian of south-western Cornwall, in the Amorican geosyncline, and in the Devonian and Lower Carboniferous of the Hartz Mountains of Germany. The Ordovician of the Green Mountain belt in Vermont and the Upper Devonian of Eastern Pennsylvania and New York (Rensselaer grit)

contain important graywacke beds. The sandstones of the Stanley shale and the Jackfork (Carboniferous) of the Ouachitas of Oklahoma and Arkansas are graywackes."

It should be noted that the Rensselaer is regarded as Lower Cambrian and the equivalent of the Rowe schist to the east by PRINDLE and KNOPF (1932, p. 284).

ESPENSHADE (1937) described similar rocks in the Badger Bay (Ordovician) series of Newfoundland as

". . . graded bedding, fine conglomerate or coarse sandstone passing into finer-grained sandstone through an interval of several feet. This rhythmical or cyclical bedding occurs in the sandstones, shales, and graywackes throughout the Badger Bay series."

KING (1949, p. 633) notes in the southern Appalachians:

"The rocks of the lower part of the Ocoee series . . . are of graywacke facies and strongly resemble the graywackes of the Archean of the Canadian Shield as described by Pettijohn . . .

"In the graywackes of the Ocoee series, as in others, graded bedding is a striking feature, which suggests that the sediments were deposited rapidly, without sorting except that which was produced by settling in water. This is manifested by cyclical arrangement of the coarse and fine deposits, each cycle beginning with granular or pebbly deposits, followed by sandy and then silty or slaty deposits, the whole cycle being represented by beds 1 ft to more than 25 ft thick, and endlessly repeated through thousands of feet of section. In many places the slaty or silty beds at the tops of the layers are broken up and reincorporated as chips or slabs in the basal deposits of the succeeding unit. Ripple marks and cross-bedding are rare."

There are undoubtedly further examples of deposits of this sort to be found in the literature of orogenic belts. It is important to be selective since the term graywacke has various definitions. Graywacke is used in the sense defined by Pettijohn in this paper (see PETTIJOHN, 1943, pp. 942–943).

Further information regarding the depositional environment of eugeosynclinal belts has been presented by BUCHER (1953, p. 275–300). He listed occurrences of fossils in metamorphic rocks and reached the conclusion that:

". . . the total number of fossils recorded after 150 years of search is too disproportionately small to allow any other conclusion, but that the larger types of fossils were rare in the original sediment . . ."

and further that

". . . it pays to emphasize the conclusion that must be drawn from the habitual scarcity of benthonic fossils, and of fossils in general, in geosynclinal sediments. A careful analysis, for which this is not the place, leaves little doubt that, of all possible factors, considerable depth of water is the one that will reduce the benthonic fauna drastically, no matter what sediment accumulates on the sea floor."

Sediment cores taken off the edge of the continent reveal remarkably few fauna with the exception of microfossils such as foraminifera. Occasional megafossils have been reported but these are primarily of shallow-water origin and have been carried down by turbidity currents or sliding. All evidence from the bottom sediments in deep water off the east coast of North America supports Bucher's argument as to the nature of the environment.

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Miogeosyncline

The sediments of the inner (miogeosynclinal) belt of the coastal plain prove to be similar in character to those of the folded Appalachians. Where exposed at the surface they are gently dipping, continental, clastic beds barren of glauconite, interbedded with glauconitic marine clastics and limestones. They are of shallow water marine or near-shore character and include lignite beds in parts. There is an increase in the calcareous content of the sediments to the south. This is also true of the sediments of the Appalachians.

There are a few deep wells in the coastal plain area which reach into the trough proper. The Hatteras Well No. 1 of the Standard Oil Company of New Jersey is one of these and shows a decrease in the percentage of non-marine sediment from that found in outcrops and from wells farther inland. Over basal clastics of possible Jurassic age are deposited Cretaceous to Recent limestones, shales, and calcareous sands with an abundant shallow-water fauna. Glauconite is common, especially in the upper part, and no lignite was noted (SWAIN, 1947, pp. 2054–2060). The log of the North Carolina Esso No. 2 shows similar lithologies. To the south, the increase in calcareous components becomes very great as illustrated by the wells described by APPLIN and APPLIN (1944, pp. 1673–1753) in Florida and adjacent states. It can be seen (*Ibid.* Figs. 22 and 23) that the clastics are more abundant to the north and to the west. It is also demonstrated that the clastic facies has been retreating and that it extended much farther on to the Florida peninsula in Cretaceous time than it does at the present time.

North of Cape Hatteras the deepest wells are west of the axis of the trough. The sediments have a larger non-marine fraction and contain a greater proportion of clastics. The Ohio Oil Company's Hammond No. 1 near Salisbury, Maryland, has lignite beds in both Miocene and Upper Cretaceous formations and a limited amount of limestone (RICHARDS, 1945, p. 903). The major part of the section is made up of sands, clays, and gravels. Well No. 1927 at the United States Naval Receiving Station, Long Beach, Long Island, New York (ROBERTS and BRASHEARS, 1946, p. 153), shows a section that is almost entirely clastic: sands, clays, and gravels, with occasional lignite beds and shells, but no limestone reported as such.

The early Paleozoic rocks of the Appalachian miogeosyncline are similar to the above. In north-west Newfoundland, Lower Cambrian arkosic and quartzose clastics are overlain by a great thickness of limestone and dolomite (KING, 1951, p. 84; SCHUCHERT and DUNBAR, 1934). In the Champlain lowland of western Vermont, limestones and dolomites make up most of the sequence up to Middle Ordovician but there are thick quartzose clastics at the base and sandy beds higher up (CADY, 1945).

"Whatever their age, the basal Cambrian sediments are invariably terrigenous. . . . The earliest Cambrian of the west flank of the Green Mountains is coarse and conglomerate in the western belts of outcrop, finer to the east." (KAY, 1951, pp. 8–9).

In the southern Appalachians the sandstones and other clastics of the Chilhowee (Lower Cambrian) are the basal deposits. The higher Cambrian contains inter-bedded shales and sandstones but the dominating rocks are carbonates. The Upper Cambrian and Lower Ordovician dolomites and limestones of the Knox group reach 4000 ft in thickness (KING, 1951, p. 121).

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The principal difference between the early Paleozoic section of the Appalachian miogeosyncline and the sediments of the present trough in the coastal plain is the more widespread distribution of carbonate rocks in the former. This difference may, to some extent, only be apparent since well logs indicate a seaward increase in the percentage of limestone. Evidence seems to point to lower elevations along the coast in early Paleozoic time with a consequent decrease in the quantities of clastic material made available. The sediments of both areas have been identified as belonging to a shallow-water environment, faunas are plentiful, and the source of the sediments was to the west. The identification of the modern trough as a miogeosyncline seems most logical.

KAY (1951, pp. 82–83) terms the depositional areas offshore from the continents "paraliageosynclines" and does not believe that they should be considered miogeosynclinal.

". . . the paraliageosynclines are believed to differ in that they mark a new cycle of subsidence in a region that has passed through an orogenic and plutonic history after having been an eugeosynclinal belt of the same general trend. Moreover, the paraliageosynclines normally pass into ocean basins, whereas miogeosynclines normally are bordered by a belt of active deformation and volcanism. Paraliageosynclines are virtually miogeosyncline-like belts of subsidence having distinctive tectonic and chronologic positions."

The writers feel that the arguments in favour of an eugeosynclinal belt off the edge of the shelf answer the objections cited above in the case of the Atlantic coastal plain area.

Geanticlinal Barrier

The division between the two troughs of the Appalachian system is marked in most places by a ridge of Pre-Cambrian rocks. These rocks are exposed in many parts of this ridge in such areas as the Green Mountains, the Hudson Highlands, the Reading Prong, the Mine Ridge anticline, and many parts of the Blue Ridge Mountains.

As mentioned earlier in this paper, it is difficult to find Pre-Cambrian rocks outside of this rather limited region. The work of Cloos, Billings, Balk, King, and others has shown that many areas, formerly considered as Pre-Cambrian, are actually Paleozoic. The presence of additional areas of Pre-Cambrian rocks is suggested by high basement velocities in the Gulf of Maine and under parts of the continental shelf. These additional areas may represent the seaward margin of the Appalachian eugeosynclinal trough and possibly the flanks of additional troughs uplifted by post-taconic activity.

The sections of Figs. 35 and 30 show that there is a definite ridge in the basement which separates the two troughs of the continental margin of the eastern United States. This ridge is present on all of the sections but varies considerably in elevation and general configuration. A similar ridge is indicated by the seismic section north-east of Recife, Brazil, and by seismic observations made on the continental margin of Argentina. The topography of the continental shelf of eastern Labrador suggests the same feature. The central part of the shelf is depressed, reaching depths of 800 meters or greater, while the outer part is mostly less than 200 meters deep. The same type of topography is present off the coast of Greenland. While there is no assurance that the topography reflects basement structure, these coastlines are not of a type which may be expected to

produce large quantities of sediment nor are marine organisms likely to produce large structures in such northern latitudes.

This ridge would be the major exposure of basement rocks following deformation, uplift, and erosion of the continental margin. There is a possibility of additional exposures on the outer margin of the continental rise trough (eugeosynclinal) due either to subsequent deformations or deeper erosion, but there should be none in or near the axis of this trough.

Base of Cambrian

One of the great problems of the Appalachian system is the location of the base of the Cambrian. The lack of fossils, structural complexity, volcanic activity, and lack of agreement on what criteria are to be used have created uncertainty which has not been satisfactorily resolved. A possible explanation for this difficulty may be gained by examining the conditions along the continental margin.

The basement rocks under the inner part of the continental shelf are metamorphosed or intruded and the contrast between these rocks and the overlying sediments is sufficiently great that there is no question as to the location of the contact. In the deep water off the edge of the shelf, the basement rocks are probably much like the overlying sediments (see section on basement velocities) with the exception that they may contain more volcanic material. Both groups are products of about the same environment of deposition and should contain the same sedimentary features.

The outer part of the shelf, however, should show a contrast between the sediments and the basement rocks even though the latter may be relatively unmetamorphosed. The sediments are of shallow water character while the basement rocks should show sedimentary features associated with a continental slope or rise environment. The contact between the two will be quite sharp if uplift was rapid and more gradational if the uplift was slow.

KING (1949, pp. 632–638) places the lower limit of the Cambrian system in the southern Appalachians between the Chilhowee series and the underlying Ocoee series on lithologic grounds. The Chilhowee series in North Carolina begins with arkosic conglomerates and sandstones, grades upward to fine-grained, indurated quartzose sandstones, and is topped by dolomite. Cross-bedding and ripple marks are common. These rocks are much like the Coastal Plain sediments which have Jurassic or Lower Cretaceous arkosic sandstones overlain by finer clastics and limestones. The Ocoee series, on the other hand, is of a different facies. The rocks of the lower part are graywackes strongly resembling those of the Archean of the Canadian Shield as described by PETTIJOHN (1943, p. 941–960). While ripple marks and cross-bedding are rarely encountered, graded bedding is common. The features exhibited by these rocks are those attributed (HEEZEN and EWING, 1952; KUENEN and MIGLIORINI, 1950, pp. 91–127; PETTIJOHN, 1950, pp. 169–171) to turbidity current deposition in deep water.

The transition is more gradual in central Virginia (BLOOMER and WERNER, 1955, pp. 579–606). The facies difference between the Ocoee and the Chilhowee is not so obvious and volcanism is not restricted to the Ocoee but is present in the lower part of the Unicoi (Chilhowee) formation. The graywackes of the Unicoi fall into the same classification as do those of the Ocoee while those of

the overlying members of the Chilhowee series do not. The Harpers formation above the Unicoi is

". . . transitional between the heterogeneous Unicoi below and the homogeneous Antietam quartzite above. . . . It consists of several hundred to more than 1000 feet of fine-grained sub-graywacke interbedded irregularly with quartzite." (BLOOMER and WERNER, 1955, pp. 595–596.)

The volcanics (Catoctin) within the Ocoee series are here classified as spilites and

". . . the cause of the secondary mineralization is more apparent than it is in some spilites (GILLULY, 1935, pp. 336–348). The albite clearly replaces andesine (An40) and does not suggest an orthomagmatic origin." (BLOOMER and WERNER, *Ibid.*, pp. 592.)

The transition is present in both areas but varies in degree. It might prove difficult to place the base of the Cambrian consistently at the same horizon on structural grounds since the rate of movement varies from place to place. The criteria suggested by KING (1949) are, however, excellent since they mark a clear distinction between two periods of orogenic activity.

Through the work of Kuenen, Heezen, Ewing, Pettijohn, and others, we have come to recognize continental slope and rise sediments by their depositional characteristics. Earlier in this paper we have seen how identification of the proper depositional environment for these sediments has provided a valuable tool for determining the original nature of the Appalachian eugeosyncline and for relating the Appalachians to the present continental margin. The above argument, with regard to the base of the Cambrian, shows that this tool is not limited to gross relationships but may be used to advantage to solve some of the details of the stratigraphy of geosynclines.

Comparison with Other Areas

A limited quantity of seismic refraction information is available from other continental margins. Some of these are quite similar to the east coast of North America; others show significant differences.

A section extending several hundred miles to sea from Recife, Brazil (Fig. 32) has been reported by WARREN and EWING (1958, in preparation). Here the sediment thicknesses are relatively small, reaching a maximum of around 8000 ft, and the width of the shelf is only a few tens of miles. With the exception of the reduction in dimensions, the basic structure is quite similar to that off eastern North America. The greatest sediment thickness is at the base of the slope, there are volcanic seamounts in deep water off the edge of the shelf, the depth to the oceanic crustal layer decreases near the base of the slope, and this layer becomes thinner under the continental rise. The basement (continental crustal) rocks form a ridge near the 100 fathom line separating the depositional trough on the shelf from that at the base of the slope and the velocity in the basement rocks decreases seawards.

Recent results off the coast of Argentina (Ludwig, personal communication) have revealed a similar structure. The shelf trough contains more than 6 km of sediment in places, but there appear to be large areas of the shelf where sediment thicknesses are of the order of 1 km. The trough off the edge of the shelf is present but its exact nature cannot be determined from the available data. The basement ridge separating the two troughs is somewhat wider than that of the

previous area. There is a ridge in the oceanic crustal layer near the edge of the shelf and a depth of 27 km to the mantle was measured on one very significant profile on the shelf. Velocities in the oceanic crustal layer approach 7 km/sec in the vicinity of the shelf edge. The area as a whole is very similar to that covered by this paper, but the more gradual slope of the bottom topography between the shelf and the ocean basin suggests a more gradual change in the depth to the mantle.

Six refraction profiles have been reported in the Gulf of Mexico between Galveston, Texas and the Yucatan Peninsula (EWING *et al.*, 1955, pp. 12–17). Fig. 31 is a modification of the resulting structure section from the above report. The Campeche Bank end of the section bears a closer resemblance to the continental margin of the eastern United States than does the Texas end. The overall bottom topography is of similar character, the profile on Campeche Bank indicates a rise in the basement surface toward the edge of the shelf, and limited magnetic data indicate anomalies near the shelf edge (MILLER and EWING, 1956). In this case, instead of a linear anomaly paralleling the coast, there appears to be a line of closed anomalies, interpreted as buried volcanoes (*Ibid.*, p. 414), along the edge of the shelf.

The Texas end of the section is quite different. If the linear anomaly is present at all, it is in the vicinity of the Texas and Louisiana coasts (*Ibid.*, p. 412). The topographic break to deep water is more gradual and has no associated magnetic effect of any magnitude. The few gravity measurements along this section reveal free air anomalies of the same order of magnitude, around 40 mgal positive, suggesting that the crustal column is of approximately equivalent mass from the basin to the shore. If the sediment–crust boundary behaves as shown (Fig. 31) and the densities agree with those used previously, the mantle must increase in depth toward the shore more gradually than is the case in the area covered by this paper.

These results indicate that, while there are continental margins which are basically the same as that of the east coast of North America north of Cape Hatteras, there are others, such as the northern side of the Gulf of Mexico, which are fundamentally different. This last area will be treated further in the next section.

COMMENTS ON MOUNTAIN BUILDING

Little is known about the forces responsible for orogenic activity. Theories have been advanced invoking both expansion and contraction of the earth, convection currents in the mantle, physical or chemical changes within the crust and mantle, movements of the crust with respect to the mantle, relative movements among portions of the crust itself, and others. Most of these are quite speculative and do not lend themselves readily to proof. Moreover, some are based on surface features which may be but minor manifestations of the principal orogenic activity.

It is not impossible that the features of orogenic belts may be explained in terms of forces which are localized in the vicinity of the belts. PAIGE (1955, pp. 331–342) has suggested that the combination of erosion and deposition with isostatic forces is sufficient to cause orogenesis.

Little can be gained by adding to the speculations above, but, if the continental margin of eastern North America is accepted as a future mountain system, it

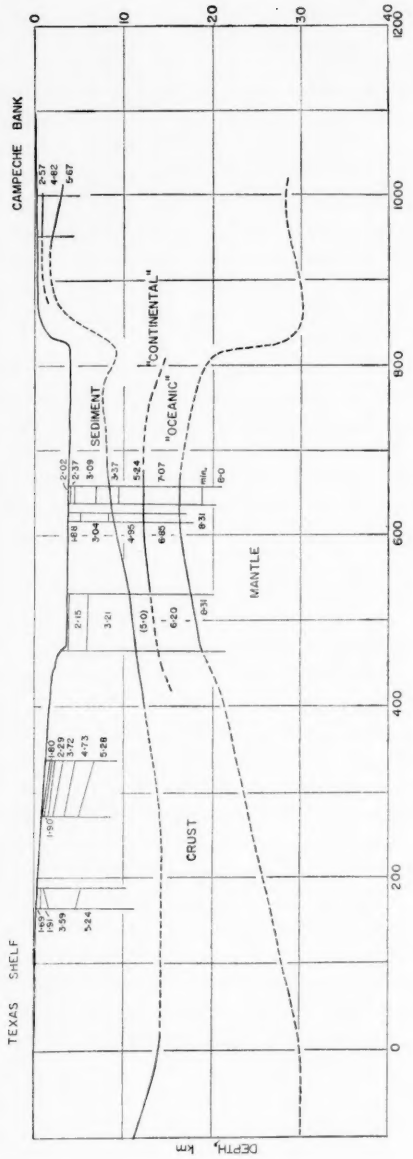

Fig. 31. Structure section—Gulf of Mexico.

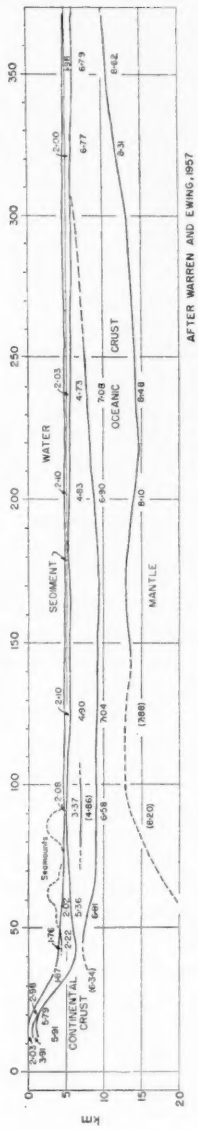

Fig. 32. Structure section—Recife, Brazil, to sea (after WARREN and EWING, 1957).

would be interesting to outline the major requirements necessary to convert it to such a system. It is also of interest to apply the results to other margins and to island arcs and to note the similarities and the differences.

Orogenic Requirements

While the miogeosynclinal sediments lie on a crust of continental thickness (Fig. 28) and sialic composition (GILLULY, 1955), the eugeosyncline is based on a crust more nearly like that of the oceans. The single most important process in an orogenic cycle must be the one which increases the crustal thickness in this area to continental proportions. Such thickening must occur in order that the area remain an isostatically compensated landmass after deformation. Seismic evidence (KATZ, 1955, pp. 303–325; TATEL and TUVE, 1955, pp. 35–50) indicates that in the plutonic and metamorphic belt of the Appalachians the crust is of continental thickness and the gravity information shows that the thick crust extends to the vicinity of the edge of the shelf.

Since the mean density of the thickened crust should approach a mean value of 2·84 g/cm^3 (Fig. 25), and since the density of the sedimentary additions will probably never exceed a maximum of about 2·70 g/cm^3, a considerable part of the thickening must be due to the addition of heavier material from below.

There is abundant evidence of such additions in the large quantities of intrusive and extrusive igneous rocks found in eugeosynclinal belts. Furthermore, the anomalous seismic velocities found in oceanic volcanic areas such as the Bermuda Rise (OFFICER *et al.*, 1952, pp. 777–808) and the Mid-Atlantic Ridge (J. EWING and M. EWING, 1957) indicates that the volcanism is accompanied by rather large changes within the crust and the mantle. These changes are such that the net effect is to increase the depth at which velocities of 8 km/sec (i.e., normal mantle velocities) are found. The same type of feature is found beneath the continental rise of eastern North America (BENTLEY and WORZEL, 1956, pp. 1–18; Table 1, this paper) but there are insufficient data at the present time to determine the extent of its development.

Many of the other features of orogenic belts may be explained in terms of this crustal thickening. Deformation of the eugeosynclinal sediments is undoubtedly due in part to slumping and sliding during the depositional stage, partly to the igneous activity, and partly to differential movements during the uplift which must occur simultaneously with or subsequent to the crustal thickening. Metamorphism of the sediments will result, after a time lag, from the heat given off by the igneous material.* The uplifted eugeosyncline will supply sediment to the miogeosyncline from the oceanic rather than the continental side. The deformation of the miogeosyncline may be attributed to plastic spreading under the influence of gravity as suggested by BUCHER (1956, pp. 1295–1318), or gravitational gliding as described by DE SITTER (1956, pp. 266–291). This process is essentially that suggested by HESS (1951, p. 528).

The relative importance of the igneous activity as compared with the sedimentary has been emphasized by HESS (1955, p. 395) who suggested that the *Taconic Disturbance* and the *Appalachian Revolution* should rightly be reversed to *Taconic Revolution* and *Appalachian Disturbance*.

* It has been noted (BUCHER, 1955, p. 359) that depth of burial and the corresponding rise of geoisotherms is not sufficient to bring about metasomatism and that the metamorphism often appears to be due to the upward passage of a heat front (KUNDIG, 1956, p. 108).

"The former was a typical alpine type of deformation, with a broad belt of metamorphosed rocks along its axis, serpentine intrusions, accompanying volcanism, and was followed by granitic intrusions. The Appalachian disturbance consisted only in the folding of the geosynclinal sediments (largely derived from the rocks squeezed up in the Taconic Revolution) situated along the western fringe of the Alpine system. The Appalachian disturbance was not accompanied by igneous activity or metamorphism. As many others have noted, it bears a somewhat analogous relationship to the Taconic mountain building that the Juras do to the Alps."

It is obvious that, in order for the above process to work, heat must be supplied. VERHOOGEN has written (1946, p. 747),

"Volcanic heat represents only a small fraction of the heat radiated by the earth . . . the real problem of volcanoes is not so much to find a suitable source of energy as to provide ways and means by which rather insignificant amounts of heat can be focused on relatively insignificant volumes of the crust."

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While this is undoubtedly true, it is necessary to know more about heat sources than is the case at the present time before the nature of the focusing can be determined. It has been suggested that the radioactive materials in a thick sedimentary column cause the heating. If this is the case, then why is heat generated in the thick eugeosynclinal section and not in the thick miogeosynclinal one? It has been suggested that a good part of the heat flow measured on the continents is due to radioactive heating in the crustal rocks. While this may be so, what is the cause of the heat flow in oceanic areas which has been found to be approximately equal in magnitude? (REVELLE and MAXWELL, 1952, pp. 199–202; BULLARD, 1954c, pp. 408–429.) BULLARD (1954a, pp. 105–122) and BENIOFF (1954, pp. 399–400) have both suggested that the heat generated by earthquakes is sufficient to produce the volcanism in orogenic belts, and there is certainly a spatial correlation between the occurrence of earthquakes and volcanoes in these belts. Owing to the time lag due to the poor thermal conductivity of rock materials (BENIOFF, 1954) and the near impossibility of knowing the seismicity of any region in the geologic past, it is difficult to evaluate this concept.

The key to the causes of orogenesis lies in the heat problem. Once the sources of the heat are determined and the method by which it is focused on small areas established, the nature of orogenic movements should be revealed. Little will be gained by proposing new theories until more knowledge has been accumulated on this subject.

Island Arcs

There are many similarities between Alpine mountain systems and island arcs. Indeed, there are island arcs which trend directly into mountain ranges with no apparent break in the structure. There are also differences both between island arcs and the mountain ranges and among the arcs themselves. Such differences are to be expected since some arcs border on continents while others do not. Those with oceanic areas on both sides, such as the West Indies or the Marianas, do not have a shallow water area upon which a miogeosyncline can form. Others, such as southern Japan and the Ryukyu Islands or the easternmost Aleutians, which do have the shallow water areas, should develop miogeosynclines.

It must be remembered that a major part of the orogenic cycle has already occurred in many island arcs. The development of the eugeosyncline into a mountain range (i.e., the equivalent of the Taconic orogeny) has taken place and, if it is to be claimed that the deep troughs represent nascent geosynclines, they must be of the eugeosynclinal type and must represent the beginnings of a new orogenic cycle. Thus, if the deeps are to be considered geosynclines, then some kind of accretion hypothesis must be accepted.

WOOLLARD (1943, pp. 806–807) has suggested that the pattern of Bouguer gravity anomalies which parallels Appalachian structural trends reflects island arc structure. A zone of negative anomalies extends from the Blue Ridge into the upper Hudson Valley and is paralleled on the east by a zone of positive anomalies (Fig. 23). These zones are relatively narrow as compared with the width of the sedimentary basins. This comparison is not unreasonable if the island area (positive) is compared with the Piedmont, and the side opposite to the deep (negative) is compared with the folded Appalachians. (See, for example EWING and WORZEL, 1954, p. 198.) The deep must be compared with the area offshore from the present coast. If the area off the edge of the shelf were stripped of its sediments, it would be a basin or trough with a maximum depth greater than 5000 fathoms and with a large negative isostatic anomaly.

This interpretation raises interesting questions concerning the formation of the geosynclinal troughs. It has been suggested that the troughs are formed by isostatic adjustment to the sedimentary load. This argument is difficult to apply to the shelf troughs since the depth of water is insufficient to allow enough sediment to be added to depress the crust. Moreover, the topography off the east coast of Labrador suggests that a shelf trough may form regardless of whether sediments are available to fill it. The argument is, however, valid for the deep water troughs since great quantities of sediment may be added without the surface of the ocean being reached. If, however, the above comparison with island arcs is accepted, then the trough may have been present prior to the sedimentation. If this were the case, the trough would be an efficient sediment trap and would prevent great quantities of continental debris from reaching the ocean basin (EWING and WORZEL, 1954, p. 172). The moderate thicknesses of sediment found in the ocean basins lend support to this interpretation.

Gulf of Mexico

The northern margin of the Gulf of Mexico is quite different from the East Coast area. From the available data it appears that, instead of an abrupt change from continental to oceanic structure near the edge of the shelf, there is a more gradual transition. Why the crust should behave in this manner and whether this behaviour reflects changes during sedimentation or the state of the crust prior to their deposition are unknown. The deepest part of the Gulf has a crustal thickness of approximately 18 km (including water), considerably thicker than the average for deep ocean basins. The basement ridge which separates the two depositional troughs of the East Coast is, if present at all, in the vicinity of the present shoreline.

Without the sharp flexure in the Mohorovicic discontinuity it seems unlikely that localized volcanism or igneous activity will develop or that the region will develop into a mountain system of the Alpine type. HESS has stated (1955, p. 401),

"Geosynclines of the Gulf Coast type seem to be comparatively rare. If one looks back over the geologic record to locate one which subsequently became a mountain system, it is hard to find one. The great thickness of sediment in the Belt geosyncline may be representative of the Gulf Coast type. Did it localize mountain building? Between the end of the Proterozoic and the end of the Cretaceous there were five or six episodes of strong deformation in North America, but none of them until the Laramide paid any attention to the Belt geosyncline. When finally this region was deformed in the Laramide it seems to have been pure chance that the orogenic movements transected the Belt."

Final Remarks

The geophysical and geological data from the continental margin of eastern North America indicate that geosynclines, such as have become mountain ranges in earlier geological times, are still being created. Such geosynclines, when uplifted and deformed, will add to the continents at the expense of the oceans by a process of accretion. A large part of the land area of the earth undoubtedly owes its existence to such a process but it is probable that the original continental nuclei cannot be accounted for in this manner. In order for a system of the Appalachian type to form there must be an adjacent land mass to supply sediments and to provide a foundation for the miogeosyncline. The original nuclei may have been primary features present when the crust solidified or secondary features resulting from igneous activity or deformation.

Until the sources of energy for mountain building are determined, it is not possible to say whether or not the above process is still continuing. Although the continental margin described in this paper bears many of the attributes of earlier geosynclines, it cannot become a mountain system unless sufficient energy can be supplied to convert it.

SUMMARY AND CONCLUSIONS

Seismic studies of the continental margin of eastern North America north of Cape Hatteras have revealed the presence of two sedimentary troughs paralleling the coast. The inner one, under the continental shelf, contains sediments up to 17,000 ft in thickness and is bounded near the edge of the shelf by a basement ridge which rises to within 4800 ft of the surface of the sediments. The outer trough, under the continental slope and rise contains a greater thickness of sediment, up to 30,000 ft off the Grand Banks of Newfoundland, which thins toward the ocean basin.

Beneath the sediments are found two crustal layers: one with velocities typical of continental basement rocks, the other with velocities in the range of those found in the crust of oceanic regions. The former lies above the latter and pinches out under the ocean basin. The oceanic crustal layer has been traced in as far as the edge of the shelf but was not found on the shelf profiles. Higher mode earthquake wave studies suggest that a continental crustal model based on two layers of approximately equal thickness is not unreasonable but the differences between the two layers may be gradational rather than sharp and may reflect changes in conditions rather than discrete layering.

The boundary between the crust and the mantle becomes obscure as the continental margin is approached from the sea. This may be due to the velocity

relations between crust and mantle and to the difficulty of producing enough energy to determine the layers accurately when they are at greater depths or to the fact that the Mohorovicic discontinuity is not a sharp boundary in this area.

Systematic velocity variations were found in some of the layers. The sedimentary velocities were found to be a function of the depth of overburden with a higher gradient occurring in the shallow water sediments than in the deep water ones. The higher shallow-water values may be attributed to the increased circulation of ground water and consequent increase in cementation or possibly to erosional effects during times when sea-level was lowered. Velocities in the continental crustal (basement) rocks decreased seaward in a systematic manner from values of about 6 km/sec near-shore to velocities of 5 km/sec or less under the continental rise. This variation is probably related to a decrease in metamorphism as the distance from the metamorphic centre of the Appalachian eugeosyncline is increased. Superimposed on this effect is a series of alternating highs and lows which appear to be structurally controlled. Velocities in the lower layers do not vary so systematically, perhaps because there are fewer data. The major effect appears to be an increase in the velocity of the oceanic crustal layer and a decrease in the mantle velocity as the continent is approached. Comparisons with oceanic volcanic areas such as the Bermuda Rise and the Mid-Atlantic Ridge suggest that there is a strong relationship between volcanic activity and crustal thickening.

Magnetic measurements across the shelf and rise revealed an anomaly of several hundred gammas amplitude paralleling the edge of the shelf that may be correlated with the basement ridge which separates the two troughs. Additional anomalies, roughly circular, were found associated with (volcanic) seamounts in the rise area. A circular anomaly of about 1000 gammas amplitude was found in 25 fathoms depth on the shelf south-east of Barnegat lightship. This, too, was attributed to a buried volcanic centre.

Evidence has been presented to show that the density is closely related to seismic compressional wave velocity and that, since there is a linear relationship between crustal thickness and elevation in oceanic regions, the ratio between crustal and mantle densities is relatively uniform. Gravity data across the shelf and rise south of Portland, Maine have been re-examined using this information and the best available seismic configuration. The results indicate a sharp change in crustal thickness from continental proportions under the shelf to dimensions more typical of oceanic areas under the continental rise. Minor variations in the densities of the layers do not appreciably change the gross picture.

The configuration of the depositional system off the east coast of North America compares very favourably with the Appalachian system as a whole as reconstructed prior to the Taconic Revolution. The shelf is similar to the early Paleozoic Appalachian miogeosyncline with sediments of shallow water origin derived from the continent and an abundance of fauna. The basement ridge resembles the Pre-Cambrian ridge (Green Mountains, Reading Prong, etc.) which separates the two depositional troughs of the Appalachians. The sediments in the outer trough are similar to the eugeosynclinal sediments of the Appalachian and other alpine-type mountain systems and resemble the graywackes of Pettijohn's classification. They are marked by a lack of shallow-water

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features and a dearth of fauna. Bucher has interpreted the scarcity of fossils in eugeosynclinal sediments as due to original scarcity rather than to destruction during metamorphism, an hypothesis which supports a deep water origin for these sediments.

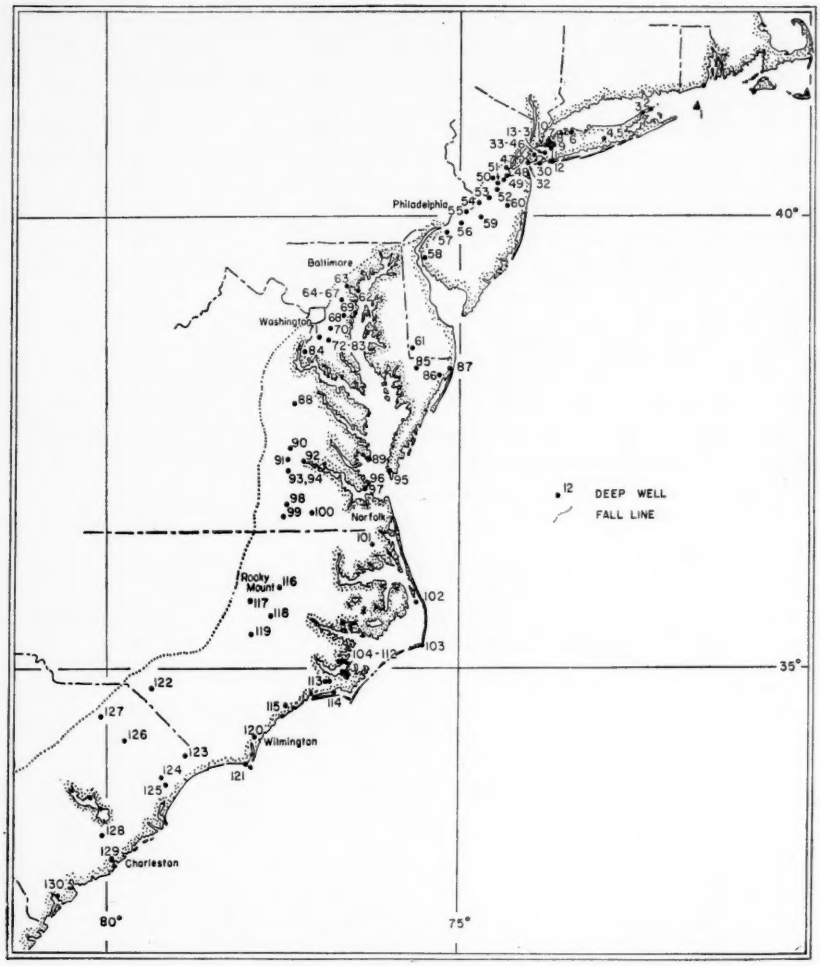

Fig. 33. Location map: wells to basement and other significant deep wells in the Atlantic coastal plain of the United States.

The decrease in metamorphism of the basement rocks, as indicated by the seismic velocities, has been shown to have an important bearing on the problem of establishing the base of the Cambrian in the Appalachians. Recognition of the depositional environment as indicated by sedimentary features enables a distinction to be made between sediments of different orogenic periods and verifies KING's (1949) criteria for determining the Cambrian–Pre-Cambrian boundary.

Comparison of the continental margin of eastern North America with other margins reveals great similarities in some cases, differences in others. The northern side of the Gulf of Mexico is quite different and Hess's conclusion that it does not represent an alpine-type geosyncline but is more comparable to the Belt system of Montana is most reasonable. Comparisons with island arcs suggest that the deeps and their associated negative gravity anomalies are best related to the outer, sediment-filled trough of the continental margin and that, if the deeps are to be considered geosynclines, some sort of accretion hypothesis must be accepted.

The major requirement to convert the continental margin to a mountain system is a process to thicken the crust under the eugeosyncline to continental proportions. This is done in part by the addition of sedimentary material from above, but at least an equal part must be contributed from below either by the addition of igneous material or the conversion of mantle to crust *in situ*. Many of the features of the Appalachian system may be explained in terms of this crustal thickening in combination with isostatic forces.

The key to understanding orogenic processes lies in the source and the method of localization of heat in orogenic belts. Should the heat be related to local phenomena, it would be unnecessary to call upon a world-wide force system to explain the deformation of these belts. Until further knowledge of the heat problem is available, it is not possible to determine the status of future mountain-building. The principle of uniformatarianism may not apply if the heat sources have changed markedly through geologic time.

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THE ORIGIN OF THE ELEMENTS

By A. G. W. Cameron

CHEMICAL COMPOSITION OF THE UNIVERSE

For many years theories of the origin of the elements have been based on the very simple assumption that there is a uniform chemical composition throughout the universe, providing one takes samples from a sufficient volume of space to include several stars. The information available concerning this presumed uniform composition was extremely scanty and usually subject to large error. The abundances of very few elements had been established to better than an order of magnitude. In such circumstances it was natural to look for one event or sequence of events in which matter had been raised to very high temperatures sufficient to form the elements in the observed proportions by various nuclear reactions.

Early estimates of cosmic abundances of the elements were based to some extent on chemical analyses of various constituents of the earth's crust. This is a very poor source of such information because not only has the earth lost most of its volatile constituents but the remaining material has been subjected to extreme chemical differentiation. Terrestrial analyses are given very little weight in recent discussions of the cosmic abundance curve (Suess and Urey, 1956).

The best sources of information concerning the abundances of non-volatile elements are chemical and radiochemical analyses of meteorites, particularly the chrondritic meteorites which Urey (1952, 1957) believes to be good samples of the non-volatile constituents of the solar system. Quite a long list of elements have had their abundances determined in the chrondritic meteorites with uncertainties of a factor two or less (Urey, 1952; Suess and Urey, 1956).

The abundances of the volatile elements must be determined from spectroscopic analyses of the light coming from stars and gaseous nebulæ. Such analyses are very difficult to make and usually require not only an accurate knowledge of atomic oscillator strengths but also the construction of good mathematical models of the stellar atmospheres which emit the lines being studied. Abundances determined from astrophysical studies have been reviewed by Greenstein (1956a) who finds that the non-volatile abundances agree fairly well with the chrondritic meteorite analyses. Goldberg *et al.* (1957), have recently made improved determinations of the abundances of many elements in the sun. The major discrepancy between their findings and the meteorite data lies in the abundance of lead, which Goldberg *et al.*, find more abundant than in meteorites by two orders of magnitude.

A semi-empirical cosmic abundance distribution of the elements constructed by Suess and Urey (1956) has played a major role in recent analyses of mechanisms of element formation. Suess and Urey made preliminary assignments of the abundances of the elements from terrestrial, meteoritic and stellar analyses. They then adjusted these so that the abundances of nuclides with odd

mass numbers fell on a smooth curve. This procedure was helped by the fact that many elements contain two isotopes with odd mass numbers; these establish the slope of the abundance curve at many places.

The writer has modified slightly the abundance curve of Suess and Urey in order to achieve a compromise with the solar data of GOLDBERG *et al.* (1957), particularly near iron and lead. The resulting abundances, plotted as a function of atomic mass number, are shown in Fig. 1.

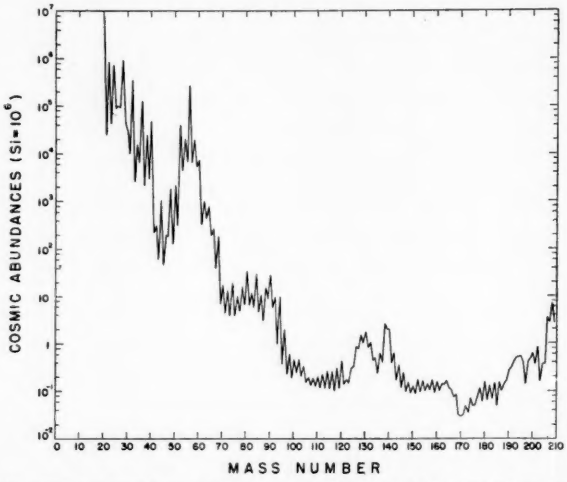

Fig. 1. The cosmic abundances of SUESS and UREY (1956) plotted as functions of mass number. The curve has been modified in the iron peak and lead regions to take partial account of the new solar abundance determinations of GOLDBERG *et al.* (1957).

Abundances of elements lighter than neon are not shown in Fig. 1. They are very individualistic. Carbon, nitrogen and oxygen are an order of magnitude more abundant than neon, but most of the abundance lies in the isotopes ^{12}C, ^{14}N and ^{16}O. The abundance of fluorine is similar to those of the minor isotopes of C, N and O. Lithium, beryllium and boron have abundances comparable to rare earth elements. The most abundant element in the universe is hydrogen. Helium is an order of magnitude less abundant than hydrogen, and the total abundance of all elements heavier than helium is two orders of magnitude less than the abundance of helium (by numbers of atoms).

It may be seen in Fig. 1 that there is a general downward trend in the abundances of the elements until about mass number 100, above which the abundance curve is very roughly flat. One outstanding anomaly in this trend is the large abundance peak centred about ^{56}Fe. Several distinctive humps may also be seen above mass number 100.

The wealth of abundance detail shown in Fig. 1 represents a great challenge to one who attempts to construct a theory of the origin of the elements. Any successful theory must not only explain the individual and general features of this curve, but, as will be shown later, it is possible to separate the naturally-occurring nuclides into different categories, and the relative abundances in these categories must also be explained by the theory. Until the work of Suess and

Urey this abundance detail was extremely unreliable, and theories of element formation usually attempted only to explain the broad general trends of the abundance curve.

While Fig. 1 has been called a "cosmic" abundance distribution of the elements, it really represents only the composition of the solar system. It is not very representative of the universe or even of the galaxy as a whole.

It appears to have been the concensus of opinion reached at the Conference on Stellar Populations, Rome, 1957, that there are at least five distinctive populations of stars in our galaxy. Forming a nearly spherical halo about the galaxy are the stars of Extreme Population II. These are stars 6 to $6{\cdot}5 \times 10^9$ years old with a heavy element content (all elements heavier than helium) of about 0·3 per cent by weight (this number seems quite variable in different stars). A slightly more flattened group of stars can be called Intermediate Population II. Here the ages range from 5 to 6×10^9 years and the heavy element content is about one per cent by weight. The stars with ages of 3 to 5×10^9 years form a highly flattened group called the Disk Population. These have heavy element contents of about 2 per cent by weight. These three populations contain 90 per cent of the mass of the galaxy. The stars with ages of 1 to 3×10^9 years are also highly concentrated toward the plane of the galaxy. These are the Intermediate Population I stars with heavy element concentrations of about three per cent by weight. Finally, there are the Extreme Population I stars, with ages ranging up to 10^9 years, which are closely associated with the spiral arms in the plane of the galaxy, usually in regions where there are heavy concentrations of interstellar gas and dust. These have heavy element contents of about four per cent by weight. The interstellar gas and dust contain about two per cent of the mass of the galaxy. They are heavily concentrated in the spiral arms, but they gradually thin out away from the plane of the galaxy, and appreciable quantities of hydrogen gas still persist at the farthest fringes of the galaxy.

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Therefore it may be seen that the heavy element content of the stars is closely correlated with their age, and that there is no such thing as a uniform chemical composition of the universe. Such other evidence that exists is consistent with the hypothesis that there is a uniform relative composition of the heavy element group. However, this is by no means certain and there is also some suggestion that there are evolutionary trends among the lighter of the heavy element group, with the nitrogen to carbon and neon to oxygen abundance ratios increasing as the age of the stars decreases.

These observations suggest very strongly that the elements heavier than hydrogen have been synthesized from hydrogen by nuclear reactions in stellar interiors, and that the products so formed have been incorporated in the newer stars.

That such nuclear reactions can take place receives observational support through the findings that certain classes of stars have very anomalous abundances of certain elements. The stars of spectral class S appear to have unusually large abundances of most elements heavier than about germanium. These heavy elements are also overabundant in a small group of stars called Ba II stars. Carbon is very overabundant in stars of spectral classes R and N, in "CH" stars, and to a lesser extent in Ba II stars and in class S. The "peculiar A" stars or spectrum variables have strong surface magnetic fields and an associated

large overabundance of heavy elements, particularly rare earths. Wolf–Rayet stars (class W) appear to be deficient in hydrogen but rich in helium, carbon or nitrogen, oxygen, and often neon. The white dwarf stars present many puzzles in peculiar abundances. Magnesium and calcium often appear to be very abundant in white dwarfs.

THE OLDER THEORIES OF ELEMENT FORMATION

Nearly all the evidence for the non-uniformity of the chemical composition of the universe has been obtained within the last three or four years. Until very recently, then, it has been customary to assume a uniform universal composition and to try to find somewhere within the framework of cosmology a set of physical conditions which would produce the elements which we observe today. Three different theories were suggested, one of them (the equilibrium theory) with many variations. The reader who is interested in the details of these theories should consult the excellent, detailed and exhaustive review article by ALPHER and HERMAN (1950). Only brief descriptions of them will be given here.

The equilibrium theories assume that at an early pre-stellar stage in the universe the matter was gathered together at high density and raised to high temperature, perhaps in massive bodies. Under these circumstances nuclear reactions take place very quickly and the detailed nuclear reaction rates are not important. Statistical mechanics tells us the relative abundances of the nuclear species provided we specify the temperature and density and that we know the energies and spins of the ground and excited states of the nuclei involved.

It turns out that for any specified temperature and density the equilibrium abundances are sharply peaked in a narrow range of mass number. Much effort has been expended in an attempt to find a massive "stellar" model which would have the correct distribution of density and temperature so that the total composition of the body would have the observed composition of the elements. One of the major difficulties with these theories is that it has not been possible to show that these massive bodies can be disrupted and cooled rapidly enough to "freeze in" the abundances of the elements with the composition characteristic of the original high densities of 10^{12} g/cm^3 or more. Nevertheless, an equilibrium theory of element formation in the interiors of presupernovæ is one of the mechanisms currently believed responsible for nucleogenesis, as will be discussed later.

MAYER and TELLER (1949) have suggested a polyneutron fission theory of the origin of the elements. Here it is assumed that the pre-stellar state of the universe contained large bodies composed of a cold nuclear fluid, mostly neutrons. The surfaces of these bodies would be unstable and would cast off polyneutron fragments in a variety of sizes. Fission, beta decay and neutron evaporation follow, and the parameters of the theory can be adjusted so that the relative isotopic compositions of heavy elements are reproduced quite well. However, it is not clear how such polyneutron bodies can arise in any cosmology or be formed in any stellar interior, and this theory does not survive in current solutions to the problem of the origin of the elements.

Another non-equilibrium theory is the neutron capture hypothesis of ALPHER *et al.* (1948), which has been extensively developed by ALPHER and HERMAN (1950). In this theory an exploding cosmological model is used which has a very high density of radiation at a very early stage in the development of the universe. The density of matter is small compared to that of the radiation; it

is broken down into neutrons and protons, and at a very early stage the relative numbers of these are fixed by the equilibrium between direct and inverse beta reactions. As the universe expands the radiation and matter cool until the neutrons can be captured by hydrogen, and it is suggested that heavy nuclei can be built up by a succession of neutron captures interspersed by beta decays. One difficulty with this theory is that there are no stable nuclei with mass numbers five and eight, so that some sort of thermonuclear reactions are required in order to bridge these gaps which neutron capture cannot cross. One has to go to such high densities to obtain such reactions (HAYASHI and NISHIDA, 1956) that the resulting theory starts to resemble quite closely that to be outlined below for stellar interiors. The neutron capture theory also fails many other detailed tests which involve the relative abundances of several different classes of heavy isotopes. Nevertheless this neutron capture theory survives in its essential features as one of the mechanisms by which heavy elements can be synthesized in stellar interiors, as will be discussed later.

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INTERCHANGE OF MATTER BETWEEN STARS AND THE INTERSTELLAR MEDIUM

The strong inverse correlation between the heavy element contents of the stars and their ages is a strong argument for nucleosynthesis in stellar interiors only if it can be shown that there is a continuous interchange of material between the stars and the interstellar medium.

The "ages" of the stars are derived in various indirect ways. Very massive stars have such high luminosities that their nuclear fuel sources must be exhausted in times short compared with the age of the universe. The age of the solar system, and presumably also of the sun, has been found to be $4{\cdot}5 \times 10^9$ years (PATTERSON, 1956) by means of the relative abundances of the lead isotopes in different meteorites. Various dynamical properties and accurate estimates of stellar masses in globular clusters have been used to date the older classes of stars. Some groups of stars are expanding away from common points in space, and it can thus be inferred that these stars were formed only a few million years ago.

It is clear that the stars are being continually formed from the interstellar medium, but the mechanism by which this occurs is still obscure. Some evidence suggests that stars are formed in clusters from dense local condensations of the interstellar gas and dust. Many "dark globules" have been observed which are suspected to be the sites of such star formation (BOK, 1948).

There are three principal ways in which stars return some of their mass to the interstellar medium. The most spectacular mechanism is the supernova explosion. In such an explosion a major portion of the stellar body is cast off into space at very high velocity, leaving a white dwarf remnant. The supernova light curve at its peak usually outshines the galaxy in which the star is situated, and about one such event occurs in an average galaxy every 300 years.

The second mechanism is the nova explosion. This is a much more superficial event (only about one part in 1000 of the stellar matter is thrown off), and correspondingly the nova explosion appears to be much less well understood than the supernova explosion. However, many if not all nova explosions are recurrent, and during the course of many explosions a substantial fraction of the stellar mass can be cast off into space.

There are also many stages in the evolution of a star in which clouds of gas can

be continuously emitted from the surface. Probably stars cast away much material in the final stages of their contraction from the interstellar medium. Much loss of matter often occurs when the star becomes a red giant. DEUTSCH (1956) has observed a case in which a class M supergiant star is emitting matter at the rate of one solar mass per 3×10^7 years or less. Even some white dwarf stars appear to be continuously emitting matter (GREENSTEIN, 1956b). These cases of continuous ejection appear to be associated with intense magnetic fields on the surfaces of the emitting objects.

The interstellar medium thus has ample opportunity to be enriched with the products of nuclear reactions in stellar interiors, and to incorporate these products in new stars. In the remainder of this article I shall show what types of nuclear reactions can take place in stellar interiors as the temperature and density are progressively increased, and that these reactions give products in approximately the proportions required in order to explain the "cosmic" abundance distribution of the elements. First it is desirable to consider some of the basic principles which underlie calculations of stellar models, and to discuss the conclusions which have been drawn concerning stellar evolution from the construction of series of models in evolutionary sequences.

STELLAR EVOLUTION

At the high temperatures characteristic of stellar interiors all except the heaviest atoms are completely stripped of electrons. The material in the stellar interior thus obeys the perfect gas laws to an excellent degree of approximation until the density becomes so high ($\gg 10^4$ g/cm^3) that electron degeneracy sets in.

There are four differential equations which determine the structure of the stellar interior. Consider a thin shell somewhere in the stellar envelope. The differential equations have the following physical content relative to this shell:

(1) Hydrostatic equilibrium: the increase of pressure across the shell must support the weight of the shell.

(2) Conservation of mass: the total mass inside the shell plus the mass of the shell is equal to the mass inside the outer boundary of the shell.

(3) Conservation of energy: the change in the net flux of energy crossing the shell is equal to the energy generated in the shell.

(4) Transport of energy: when the temperature gradient is small energy transport takes place entirely by radiation; the temperature gradient is then proportional to the opacity of the material. For high temperature gradients energy transport by convection sets in. Under such conditions the volume elements suffer nearly adiabatic displacements and the temperature, pressure and density are given to a good approximation by the adiabatic relationships.

These differential equations must be supplemented by certain physical relations between the variables. The total pressure in the gas is equal to the sum of the gas and radiation pressures. The stellar opacity must be calculated from atomic theory. The rate of energy generation is the sum of contributions due to gravitational contraction and thermonuclear reactions. The latter must be obtained from nuclear theory and from experiment.

With these equations it is possible to take an initial configuration of gas and to follow changes in its structure and chemical composition as a function of time. Electronic computers must be used in order to obtain accurate results; so far only preliminary results of such calculations are available (HENYEY, 1957;

HASELGROVE and HOYLE, 1957). However, the general nature of these results has been known for some time from work with simplified mathematical models of stellar interiors (HOYLE and SCHWARZSCHILD, 1955).

When a star is formed from a local condensation of the interstellar gas and dust, it must get rid of most of the magnetic field associated with the material when it was part of the interstellar medium. It is likely that a certain loss of mass accompanies the loss of the magnetic field, perhaps in the late stages of the contraction.

During the contraction the interior of the star is heated by the release of gravitational potential energy. When the temperature reaches about 10^{6}°K the deuterium is destroyed by thermonuclear reactions with itself, and with hydrogen (SALPETER, 1955). At about 3×10^{6}°K, 4×10^{6}°K and 7×10^{6}°K, respectively, the lithium, beryllium and boron isotopes are destroyed by thermonuclear reactions with hydrogen. The products formed by all these reactions are helium isotopes. At slightly higher temperatures the hydrogen starts to react with itself in the proton–proton chain of reactions. These reactions are:

$$^{1}\mathrm{H}(p, \beta^{+}\nu)^{2}\mathrm{D},$$

$$^{2}\mathrm{D}(p, \gamma)^{3}\mathrm{He},$$

$$^{3}\mathrm{He}(^{3}\mathrm{He}, 2p)^{4}\mathrm{He}.$$

At higher temperatures the ^{3}He concentration becomes small and the proton–proton chain branches to undergo the reactions:

$$^{3}\mathrm{He}(\alpha, \gamma)^{7}\mathrm{Be}$$

$$^{7}\mathrm{Be}(e^{-}, \nu)^{7}\mathrm{Li}(p, \alpha)^{4}\mathrm{He} \quad \text{(free electron capture)}$$

or

$$^{7}\mathrm{Be}(p, \gamma)^{8}\mathrm{B}(\beta^{+}\nu)^{8}\mathrm{Be}(\alpha)^{4}\mathrm{He}.$$

For stars which have about 1·5 times the mass of the sun, or less, the central temperature will increase to about 17×10^{6}°K, or less for smaller masses, and the proton–proton reactions will then release energy at a sufficient rate to maintain the full luminosity of the star. The star stops contracting and is stable for a long period of time until the hydrogen at its centre becomes depleted. The star is said to belong to the main sequence. The oldest stars are still in the main sequence if their masses do not exceed about 1·25 solar masses, since they have not had time to exhaust their central hydrogen.

The more massive stars continue their initial contraction until the central temperature exceeds 17×10^{6}°K. At these higher temperatures a new set of thermonuclear reactions provides more energy generation than the proton–proton chain. These reactions form the carbon cycle:

$$^{12}\mathrm{C}(p, \gamma)^{13}\mathrm{N}(\beta^{+}\nu)^{13}\mathrm{C},$$

$$^{13}\mathrm{C}(p, \gamma)^{14}\mathrm{N},$$

$$^{14}\mathrm{N}(p, \gamma)^{15}\mathrm{O}(\beta^{+}\nu)^{15}\mathrm{N},$$

$$^{15}\mathrm{N}(p, \alpha)^{12}\mathrm{C}.$$

In these reactions the carbon and nitrogen nuclei act as catalysts for the conversion of hydrogen into helium. The equilibrium abundance of ^{14}N is much

higher than the equilibrium abundances of the other carbon and nitrogen isotopes.

Stars with several solar masses will burn their central hydrogen at temperatures of about 30×10^6°K. The carbon cycle will turn over many times while these stars are on the main sequence, and during this time the abundances of certain other light nuclides will be changed. The oxygen isotopes and ^{19}F will be largely transformed into carbon cycle nuclei.

When the central regions of a star are largely depleted of hydrogen, its luminosity starts to increase slowly. After complete exhaustion of the hydrogen at the centre the star contracts sufficiently to raise the central temperature enough to start burning hydrogen in a shell around the inert core. After the shell has burned for some time and the inert core has grown until it contains more than some 12 per cent of the stellar mass, the core starts contracting and the outer envelope expands enormously. The star is now a red giant.

At this stage the temperature in the hydrogen-burning shell is in the range 40 to 60×10^6°K. This temperature may possibly be high enough to transform the abundances of some of the neon and sodium isotopes, but this point is very uncertain. The density of material in the core reaches 10^5 g/cm^3. The electrons then form a degenerate gas with some unusual physical properties. Its equation of state is quite unlike that of an ordinary gas; when a degenerate gas is compressed its temperature falls, and an expansion of the gas results in an increase in its temperature.

When about 50 per cent of a star of about 1·3 solar masses has been exhausted of hydrogen, the temperature at the centre of the helium core reaches 10^8°K. Helium thermonuclear reactions then set in. The degenerate gas at the centre is highly unstable in the presence of these reactions, and a structural change is forced upon the star in which the core expands and the outer envelope probably collapses to some extent. A considerable amount of internal mixing between the helium and hydrogen regions of the star may occur at this time.

The further evolution of the star has not been followed yet by calculations involving sequences of stellar models. Only the final result is known: the stars eventually become white dwarfs. These are very dense stars, containing no nuclear energy sources, in which the electrons form a degenerate gas throughout nearly all the volume. The average mass of the white dwarf stars is about 0·6 solar masses (GREENSTEIN, 1957), and it is known theoretically that the mass of a white dwarf cannot exceed about 1·25 solar masses. These stars gradually cool by radiating away their internal heat energy, but this is a slow process which takes a long time compared with the age of the universe.

It can thus be seen that stars must lose mass in advanced stages of their evolution before they become white dwarfs. Some of the mass is often lost by continuous ejection in the red giant stage. Some stars lose mass in nova and super-nova explosions, and there are many other peculiar classes of stars which lose mass by continuous ejection at late stages of their evolution.

The evolutionary sequence of stellar models has been carried only to the point at which helium thermonuclear reactions commence. It is not possible to extrapolate the sequence of models in any way owing to the major structural changes which take place when the helium reactions start. Hence in considering these reactions it is necessary to proceed in a more general way and to see what happens at various temperatures and densities which seem reasonable.

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HELIUM THERMONUCLEAR REACTIONS

A pure helium gas is stable in a thermonuclear sense until very high temperatures (10^{8}°K) are reached, because the product formed when one alpha-particle captures another, ^{8}Be, is unstable, and breaks down in about 10^{-16} sec:

$$2^{4}\text{He} \rightleftharpoons {}^{8}\text{Be}$$

However, at 10^{8}°K in a stellar core with a density of 10^{5} g/cm^{3}, the helium collisions are sufficiently energetic and frequent to maintain a small amount of ^{8}Be in the gas (about 1 part of ^{8}Be to 10^{8} parts of ^{4}He).

The second excited state of ^{12}C nucleus is resonant in the optimum range of alpha-particle bombarding energies for the conditions we are considering. This state is therefore relatively easily formed despite the small equilibrium abundance of ^{8}Be. Most of the time this state decays back into ^{8}Be and ^{4}He, but occasionally it emits electromagnetic radiation and ^{12}C is formed (Cook *et al.*, 1957; Salpeter, 1957):

$$^{8}\text{Be}(\alpha, \gamma)^{12}\text{C}.$$

The carbon formed in this way can undergo a series of alpha-particle captures

$$^{12}\text{C}(\alpha, \gamma)^{16}\text{O},$$

$$^{16}\text{O}(\alpha, \gamma)^{20}\text{Ne},$$

$$^{20}\text{Ne}(\alpha, \gamma)^{24}\text{Mg}, \ldots$$

Only rarely does the last of these reactions take place.

The behaviour of the helium reactions under different conditions of temperature and density is quite variable and depends on nuclear parameters whose values are not yet known. However, certain aspects of this behaviour appear to be clear (Burbidge *et al.*, 1957; Cameron, 1957c).

Very luminous stars which consume helium at a fast rate, producing 10^{6} ergs/g sec or more in the helium gas, form almost entirely ^{12}C during the course of these reactions. In somewhat less luminous stars ^{12}C will be the main product during the early stages of the helium consumption, but this will then be consumed and the final product will be mostly ^{16}O. Still fainter stars in which helium reactions produce perhaps 10^{2} ergs/g sec will form nearly pure ^{20}Ne as the final product. Of course it is quite possible to obtain variations in this behaviour by changing the conditions in which the helium is consumed. For example, if the energy release in the gas stays at a very high level until about ninety per cent of the helium is consumed, and then drops to a low level, the final products will be a mixture of ^{12}C and ^{20}Ne, with very little ^{16}O.

It seems likely that these helium reactions have been responsible for creating the excess carbon and the excess neon which many stars exhibit in advanced stages of evolution. These thermonuclear products may appear in the surface layers as a result of extensive mixing processes triggered by degenerate instabilities, or they may also perhaps be seen after a star has cast away into space most of its outer layers.

Certain other helium thermonuclear reactions are of interest because neutrons are produced by them. Two reactions have been suggested as copious sources

of neutrons. The first of these (GREENSTEIN, 1954; CAMERON, 1954) is the reaction

$$^{13}C(\alpha, n)^{16}O.$$

CAMERON (1955; 1957b; 1957c) has suggested that this reaction will be particularly important where there is internal mixing in a star where helium thermonuclear reactions have commenced, perhaps accompanying the initial structural rearrangement of the star. In this hypothesis ^{12}C produced in the core reacts with hydrogen mixed in from the envelope to produce ^{13}C. This may subsequently react with helium to produce neutrons.

The second suggestion (FOWLER *et al.*, 1955a; MARION and FOWLER, 1957) is that neutrons are produced by the reaction

$$^{21}Ne(\alpha, n)^{24}Mg.$$

The basis for this suggestion is that the bulk of the ^{20}Ne originally present in the star may have been converted to ^{21}Ne by the reactions

$$^{20}Ne(p, \gamma)^{21}Na(\beta^+\nu)^{21}Ne.$$

This requires rather high temperatures which can possibly be supplied in the hydrogen-burning shell sources in giant stars. At the present time it is not known whether the reaction rate for proton capture by ^{20}Ne is large enough for the reaction to occur. If it is, then it is not known whether the ^{21}Ne will be destroyed or not by the reaction

$$^{21}Ne(p, \gamma)^{20}Na(\beta^+\nu)^{22}Ne.$$

If this reaction also has a large cross-section then neutron production would be correspondingly diminished.

NEUTRON CAPTURE ON A SLOW TIME SCALE

The $^{13}C(\alpha, n)^{16}O$ reaction probably produces neutrons at temperatures near $1 \times 10^{8\circ}K$, the $^{21}Ne(\alpha, n)^{24}Mg$ reaction near $1{\cdot}6 \times 10^{8\circ}K$. In either case the neutrons are released into a medium in which their scattering cross-sections are very large compared to their absorption cross-sections. They are therefore slowed down until they are in thermal equilibrium with their surroundings. At a temperature of $10^{8\circ}K$ the neutron energies then lie in the vicinity of 10 keV. They are captured by the surrounding nuclei in proportion to their neutron capture cross-sections averaged over the Maxwell distribution of neutron energies.

There are very few experimental measurements of neutron capture cross-sections in the kilovolt range. It is therefore necessary to use the systematic statistical properties of nuclei in calculating the necessary cross-sections. The writer has made preliminary calculations of this kind (CAMERON, 1957c), and has solved the abundance differential equations to determine how nuclide abundances change as neutrons are captured by an initial "cosmic" abundance distribution, as shown in Fig. 1.

This neutron capture process occurs on what is called the slow time scale. The mean time between neutron captures by a typical heavy nucleus can range anywhere from 1 to 10^5 years; this is much slower than another neutron capture process to be described later. A nearly unique capture path is associated with

the process. When a neutron capture product is radioactive, it usually has time to decay before the nucleus can capture another neutron, although a few radioactive nuclides such as ^{99}Tc have half-lives long compared with the neutron capture time scale and hence are "stable" members of the neutron capture path. The upper end of the capture path is terminated at ^{209}Bi, because neutron capture beyond this nucleus leads to alpha-particle emitters with half-lives very short compared with the neutron capture time scale; hence neutron capture products accumulate as lead and bismuth isotopes.

A typical set of results from these calculations is shown in Fig. 2. The solid circles in this figure represent the original cosmic abundance distribution assumed

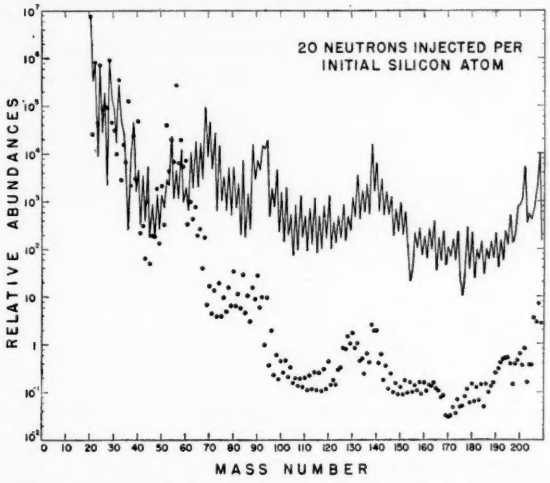
20 NEUTRONS INJECTED PER
INITIAL SILICON ATOM
RELATIVE ABUNDANCES
MASS NUMBER
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

Fig. 2. The abundances produced by the capture of twenty neutrons injected per initial silicon atom. The ordinates correspond to an initial abundance of 10^6 silicon atoms. The initial abundances are indicated by solid dots.

to be present in the stellar core. The first neutrons are captured predominantly by the nuclei in the iron peak. As the capture progresses some of the original iron peak nuclei move up into the heavy element region. By the time that twenty neutrons have been captured by the heavy elements for every silicon atom initially present, as in Fig. 2, the heavy elements have become overabundant by a factor of 1000 or more.

One feature of Fig. 2 which is particularly significant for the later analysis of nuclide abundances is the ratio of the general abundance level near mass number 120 to that near mass number 170. This ratio varies only between about two and ten during the entire course of the neutron capture.

The above results are correct only if one ignores the competition of ^{14}N with the heavy elements for the neutrons. The ^{14}N$(n, p)^{14}$C reaction is exothermic and hence has a rather large cross-section. The writer has shown (CAMERON, 1957a; 1957c) that if ^{13}C is the main source of neutrons and is produced by a mixing process, then large overabundance factors are attained by the heavy elements only when the amount of hydrogen mixed into the core is small compared to the amount of ^{12}C there. Otherwise the carbon cycle reactions produce

too much ^{14}N. If ^{21}Ne is the main neutron source this difficulty probably does not arise, because the ^{14}N may be destroyed by helium reactions at a lower temperature than that at which the neutrons are produced.

It seems likely that the heavy elements observed to be very overabundant in S stars and in Ba II stars have been formed by neutron capture on a slow time scale. The presence of technetium in S stars in abundance comparable to its neighbouring elements shows that these stars have contained neutron sources within the recent past, since ^{99}Tc is the only isotope of this element on the neutron capture path, and it has a half-life of 210,000 years. BURBIDGE and BURBIDGE (1957) have determined heavy element abundances in one of the Ba II stars and have shown that the overabundance factors are consistent with neutron capture on a slow time scale.

Although these neutron production reactions are very important in considerations of nucleogenesis, they are not important as sources of energy generation, and most of the helium in a star is consumed by the principal helium reactions described earlier. The last five per cent or so of the central helium is not consumed until the central temperature of a star increases into the range 2 to 3×10^{8}°K. The material at the centre is then inert, and helium consumption may perhaps occur in a shell source.

HEAVY ION AND PHOTONUCLEAR REACTIONS

After the helium is exhausted in a stellar core the material remains inert until temperatures of nearly 10^{9}°K are reached. If stellar interiors can reach such a high temperature, then two new classes of reactions become possible. One class of reactions is called here "heavy ion" thermonuclear reactions, since it describes reactions among the carbon, oxygen and neon nuclei which have remained after the helium has been exhausted. Such reactions form compound nuclei of intermediate mass at fairly high excitation energies, usually above the binding energies of one or more of a neutron, proton or alpha-particle, which will be emitted as a product of the reaction,

The second class of reactions consists of photodisintegration processes in which alpha-particles are removed from such light nuclei as ^{16}O and ^{20}Ne by photons in the high energy tail of the Planck distribution function corresponding to the temperature of the stellar interior.

The general effect of these various reactions is to synthesize nuclei in the range from neon to calcium (HOYLE, 1954; BURBIDGE *et al.*, 1957). There are many different reactions involved here, and the interactions between the various processes have not yet been worked out in detail, so that abundances in this range cannot yet be compared with a detailed theory.

The heavy nuclei formed by neutron capture on a slow time scale are also subject to photodisintegration when the temperature rises above $1{\cdot}3 \times 10^{9}$°K. In this case neutrons are emitted, and the resulting nuclei will usually undergo radioactive decay before a second neutron can be removed. However, a few heavy nuclides are formed in this way which cannot be formed by neutron capture; they form part of the class of excluded isobars to be discussed later.

Thus in this temperature range both the light and the heavy nuclei are destroyed by reactions which produce products closer to the medium range of mass numbers. This trend is accelerated if still higher temperatures can be reached and equilibrium conditions approached.

EQUILIBRIUM REACTIONS AND SUPERNOVA EXPLOSIONS

If the temperature in a stellar core can rise above 3×10^{9}°K, then a great variety of nuclear reactions can occur with very rapid rates. The abundances of the nuclides are then calculable from statistical mechanics. It is here that the older theories of element formation under equilibrium conditions find their place.

At temperatures below about 5×10^{9}°K and densities of the general order of magnitude of 10^{4}–10^{6} g/cm^{3} the most abundant nucleus in statistical equilibrium is ^{56}Fe. If the density is increased by several orders of magnitude somewhat heavier nuclei become most abundant. However, if the temperature is raised above 5×10^{9}°K, then ^{4}He becomes the most abundant nucleus, with a small range of conditions in which the material changes from being nearly all ^{56}Fe to being nearly all ^{4}He.

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Some of the nuclides with fairly large equilibrium abundances are radioactive and decay by electron or positron emission or electron capture. In each such decay a neutrino or antineutrino is released which escapes from the star with negligible nuclear interaction, carrying away energy directly from the core. This is a powerful cooling mechanism which promotes the slow collapse of the central regions of the star, thus raising the central temperature. It is the "urca" process of GAMOW and SCHOENBERG (1941).

^{56}Fe is the most abundant nucleus at this point because it has the largest binding energy per nucleon of any nucleus. The net result of all the thermonuclear reactions which form ^{56}Fe out of hydrogen is to release energy, some of which is stored as the internal heat content of the star and the remainder of which is radiated into space. Thus when the central temperature crosses the critical dividing point beyond which ^{4}He must become the most abundant nucleus, there is no nuclear energy source available to cause the endothermic conversion of iron to helium. The only available energy source is the gravitational potential energy of the material in the core. Hence the production of helium must be accompanied by the collapse of the inner stellar core, and this collapse will take place in a time of just a few seconds (HOYLE, 1946).

When the inner support is removed from the stellar envelope, it too will collapse toward the centre of the star, being heated by the release of gravitational potential energy. This material may have a very varied composition. It may contain the products of many different thermonuclear reactions which have been mixed through the star. In any case, there will be plentiful nuclear energy sources in all but the innermost parts of the envelope, and when this material is suddenly heated to 10^{8}°K or more the hydrogen and helium thermonuclear reactions will accelerate very quickly and will release an enormous amount of energy. The outer layers of the star will then be blown off with high velocities in a supernova explosion, leaving behind a white dwarf star.

The innermost parts of the envelope which had not previously attained nuclear statistical equilibrium are nevertheless likely to have been too hot to contain hydrogen. Part of this region is likely to be raised above 3×10^{9}°K in the collapse, and the resulting energy release will suffice to remove it into space. However, in the meantime statistical equilibrium will have been established in it, and this equilibrium will be preserved in somewhat distorted form when the temperature falls below some critical temperature at which the nuclear reactions become slower than the rate of expansion of the exploding envelope.

BURBIDGE *et al.* (1957), have calculated the equilibrium abundances to be expected following the "freezing-in" process. Their results are given in Fig. 3 where they are compared with the solar abundance determinations of GOLDBERG *et al.* (1957). It may be seen there is a close correspondence between the relative isotopic abundances except on the fringes of the diagram, and there is nearly as good an agreement between the relative abundances of the elements. Thus the iron peak in the cosmic abundance distribution appears to have been formed in supernova explosions.

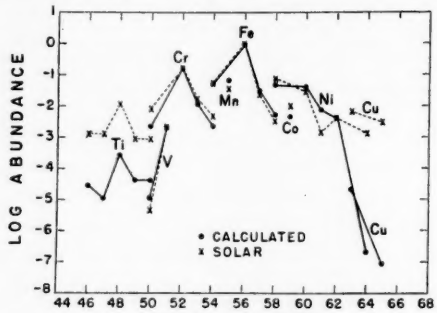

Fig. 3. The frozen equilibrium abundances calculated by BURBIDGE *et al.* (1957), for a temperature of $3{\cdot}8 \times 10^{9}$°K and a proton to neutron ratio of 300. These are compared to the solar abundances of GOLDBERG *et al.* (1957). Both sets of data are normalized to unity at ^{56}Fe.

Although there are very many reactions which can take place in a supernova envelope during the explosion, the course of these reactions depends in a critical way upon the composition of the envelope. The most important constituent is hydrogen, and quite different results are produced in cases where the hydrogen is in large or small abundance compared to other light elements. These results are discussed in the following two sections.

NEUTRON CAPTURE ON A FAST TIME SCALE

In this section the case in which the hydrogen abundance is less than or equal to the abundance of other light nuclei (apart from helium) is considered. It is assumed that these light nuclei are the products of earlier thermonuclear reactions in the star.

At the start of the explosion the hydrogen will be rapidly consumed in reactions with the light elements. Following the exhaustion of the hydrogen the proton capture products will usually be unstable to positron emission and have half-lives of some seconds, comparable to the duration of the explosion. Among the products formed in this way will be the $4n + 1$ series ^{13}C, ^{17}O, ^{21}Ne, etc. These nuclei will interact with alpha-particles to produce neutrons in exothermic (α, n) reactions. We shall be interested in the formation of heavy elements with these neutrons.

BURBIDGE *et al.* (1956), and BURBIDGE *et al.* (1957), suggest that ^{21}Ne (α, n) ^{24}Mg is the most important source of neutrons because it has the lightest $4n + 1$ precursor with a half-life comparable to the duration of the explosion (23 sec ^{21}Na). However, there are considerable difficulties with this view, since all

the positron emitters formed simultaneously with ^{21}Na can undergo exothermic (n, p) reactions with rather large absorption cross-sections. Since these positron emitters are probably formed with greater abundances than the neutron precursors, it appears doubtful that much heavy element formation would occur in competition with the (n, p) reactions.

The writer (CAMERON, 1957c) has suggested that neutron production will be most important in those supernovæ which have considerably more ^{12}C than hydrogen in their envelopes. We have seen that this can be a reasonable set of conditions following the helium reactions. At the start of the explosion the hydrogen reacts almost entirely with the ^{12}C which gives the fastest reaction. The resulting ^{13}N nuclei have a half-life of 10 min and in the first 10 sec following hydrogen exhaustion 1 per cent of them will decay to ^{13}C. The neutrons then produced by the ^{13}C (α, n) ^{16}O reaction will be mostly captured by ^{13}N, giving the reaction

$$^{13}\mathrm{N}\ (n, p)^{13}\mathrm{C}$$

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This regenerates ^{13}C and hence maintains the supply of neutrons. The protons released in the process again react principally with ^{12}C to regenerate ^{13}C. In this way a high flux of neutrons will be maintained until the ^{12}C is exhausted, and then the neutron flux will be terminated quite sharply by other (n, p) reactions which do not lead to neutron regeneration.

During the period of neutron production a flux of something like 10^{32} neutrons/cm^2 sec will exist in the reacting layers, and the temperature may be about 4 or 5×10^{8}°K. Under these conditions the nuclides of intermediate and heavy mass will capture neutrons very quickly. As successive neutrons are captured the neutron binding energy gradually decreases. Eventually, when the neutron binding energy has fallen to about 2 MeV, the rate of photoneutron emission becomes equal to the rate of neutron capture. The nuclei then wait until beta decay occurs. The nuclei at this point are far out on the neutron-rich side of the valley of beta stability on the nuclear mass surface. The beta-decay energies are therefore quite large, usually 10 or 15 MeV, and the writer estimates that the beta decay will have a half-life of usually less than 1 sec. BURBIDGE *et al.* (1957), estimate that in many cases among the lighter elements the half-life will be an order of magnitude larger. Following beta decay, neutron capture takes place again until the neutron binding energy is reduced to about 2 MeV once more. This process is illustrated by Fig. 4, which shows the path followed by an original ^{56}Fe nucleus as it captures a succession of neutrons and beta decays when the neutron binding energy falls to 2 MeV. This path has been calculated from a semi-empirical atomic mass formula developed by the writer (CAMERON, 1957d).

When complete shells of neutrons are filled at neutron numbers 50, 82, 126 and (by assumption) 184, the neutron binding energy decreases by about 2 MeV more than usual. Hence the number of neutrons in the nucleus cannot increase beyond the closed shells until a series of beta decays has brought the nucleus closer to the valley of beta stability than usual. This produces the vertical "ladder" sequences at the neutron closed shells which are shown in Fig. 4.

Although the neutron capture path is shown passing off the diagram at the upper right in Fig. 4, it is not expected that the nuclei will build up quite so far. Neutron capture will be terminated by fission somewhere in the heavy element

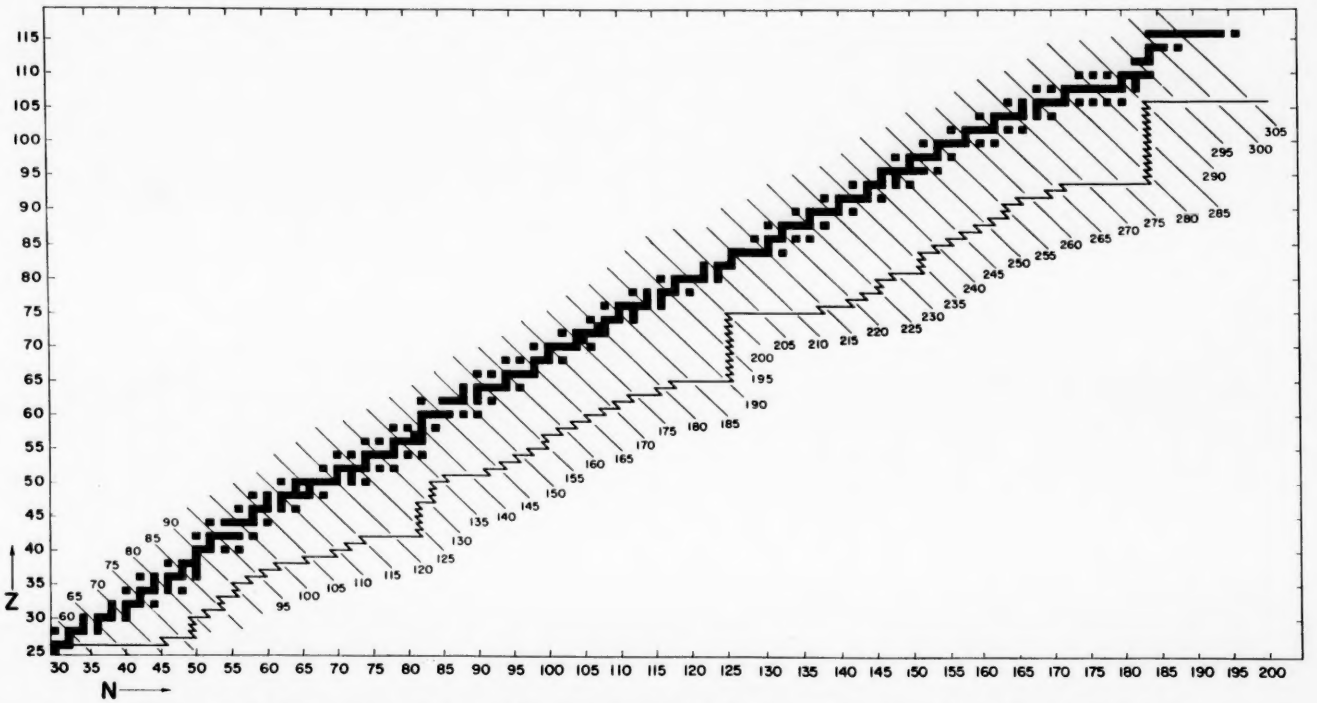

Fig. 4. A nuclide chart showing the path of neutron capture on a fast time scale constructed on the assumption that photodisintegration will prevent neutron capture when the neutron binding energy falls below 2 MeV. The black squares show beta stable nuclides. The diagonal lines show mass numbers.

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region. The writer believes (CAMERON, 1957c) that fission will occur near the upper end of the ladder at 184 neutrons when the neutron capture leads to the vicinity of the nucleus $^{287}103$. BURBIDGE *et al.* (1957), argue that the fission will occur at about mass number 260. These differences arise because of the difficulties in extrapolating fission systematics into the very heavy element region. The two fission fragments continue to capture neutrons and to move up the capture path again.

When neutron captures and photodisintegrations cease, the neutron-rich nuclei quickly decay toward the valley of beta stability. The nuclei of mass number 254 are of particular interest. Beta decay quickly transforms them into the nuclide ^{254}Cf, which decays predominantly by spontaneous fission with a half-life of $56{\cdot}2 \pm 0{\cdot}7$ days (HUIZENGA and DIAMOND, 1957). It appears likely that, when the gas from the exploding envelope forms a dilute "nebula" around the star a few months after the explosion, the decay of ^{254}Cf will yield much more energy than will be obtained from the decay of any other product with a half-life lying between a few days and a few years. Baade has carefully observed the light curve from the supernova in the galaxy IC 4182 (BAADE *et al.* 1956). This curve was observed to have an exponential tail with a half-life of 55 ± 1 days.

There are two classes of supernovæ. Type I supernovæ exhibit a fifty-five day exponential tail and seem to be associated with the Population II stars. It is tempting to believe that neutron capture on a fast time scale has taken place in these stars. Type II supernovæ do not show an exponential tail. They appear to be associated with the younger stars of Population I.

FAST REACTIONS IN HYDROGEN-RICH ENVELOPES

We will now consider what happens in a supernova explosion when the abundance of hydrogen is much greater than that of the other light elements. When the explosion starts the light elements capture one or more protons until the proton binding energy falls and the rates of proton capture and photoproton emission become equal. The nuclei then wait until positron emission occurs, after which more proton capture can take place. This is analogous to neutron capture on a fast time scale, but there are complications owing to (p, α) and (α, p) reactions in the light elements.

The hydrogen will usually not become exhausted during the explosion, and hence only infinitesimal amounts of nuclei such as ^{13}C of ^{21}Ne will be formed. Thus neutron production does not take place. The total energy generation in the envelope will be smaller than that accompanying neutron production.

If the temperature in the exploding layer rises as high as 2×10^{9}°K, then proton capture can extend into the heavy element region. This will form some beta stable nuclei on the neutron-deficient side of the valley of beta stability which cannot be formed by neutron capture on any time scale.

However, when the temperature reaches the range $2{\cdot}0$–$2{\cdot}5 \times 10^{9}$°K, photoneutron emission sets in with emission half-lives comparable to the period of explosion. In this way also some neutron-deficient nuclides can be formed.

It is tempting to believe that supernovæ of Type II contain hydrogen-rich envelopes in which the reactions described here will take place. The light curves of these supernovæ do not contain exponential tails because there has been no formation of ^{254}Cf.

The high temperature equilibrium reactions and the fast time scale supernova

reactions appear to be the extremes of behaviour likely to take place in stellar interiors. Therefore it is time to consider in detail the cosmic abundance distribution of the nuclides and to see if the reactions which have been described can account for these details.

ANALYSIS OF NUCLIDE ABUNDANCES

Main sequence stars and also red giant stars obtain their energy from the conversion of hydrogen into helium. The large natural abundance of ^{4}He can readily be produced in this way. The very abundant nuclides ^{12}C, ^{16}O and ^{20}Ne are the main products of the helium thermonuclear reactions. A great deal of ^{16}O may also be produced by the ^{13}C(α, n)^{16}O reaction in Type I supernovæ.

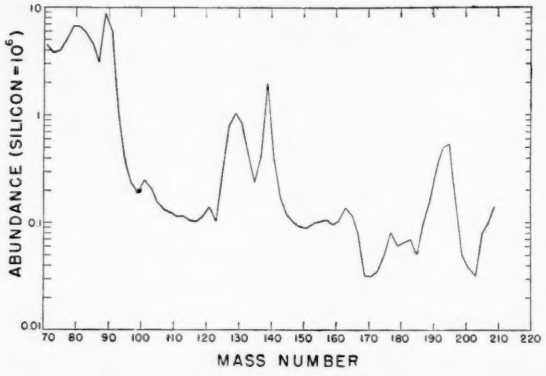

Fig. 5. The abundances of heavy nuclides with odd mass numbers according to SUESS and UREY (1956).

The nuclides ^{13}C and ^{14}N can be produced in the observed abundances by carbon cycle reactions which make use of ^{12}C and ^{16}O produced by helium reactions. ^{18}O, ^{19}F and ^{22}Ne can be formed from ^{14}N and ^{15}N by helium reactions. The nuclides ^{15}N, ^{17}O and ^{21}Ne can be formed by proton capture reactions which operate on both fast and slow time scales.

There is a variety of mechanisms by which the nuclei in the range neon to calcium or titanium can be produced. These mechanisms include neutron capture on both slow and fast time scales, heavy ion thermonuclear reactions on both slow and fast time scales, and hydrogen and helium reactions on a fast time scale. At present it is very difficult to disentangle the effects of these various reactions, but the cosmic abundance distribution does appear to be consistent with the abundances of the reaction products which are likely to be formed.

We have seen that BURBIDGE *et al.* (1957), have given a good quantitative explanation of the iron abundance peak as resulting from equilibrium reactions at high temperatures and densities.

Beyond the iron peak only a few mechanisms are effective in synthesizing heavy elements, and it is possible to analyse the abundances to determine how effective these mechanisms have been. Figure 5 shows the abundances of the nuclides with odd mass number according to SUESS and UREY (1956). It may be seen that this distribution contains several major peaks.

Abundance peaks can be expected at about mass numbers 90, 140 and 209, corresponding to the formation of nuclei with closed shells of 50, 82 and 126 neutrons by neutron capture on a slow time scale. The neutron capture cross-sections of closed shell nuclei are much smaller than those of their neighbours and hence the equilibrium abundances are larger. It may be seen that these peaks exist in the abundance plot of Fig. 5 (the peak at mass number 209 should be much larger than shown if one believes the larger solar abundance of lead).

In neutron capture on a fast time scale the path (shown in Fig. 4) cannot cross the closed neutron shell positions until beta decay has brought the path

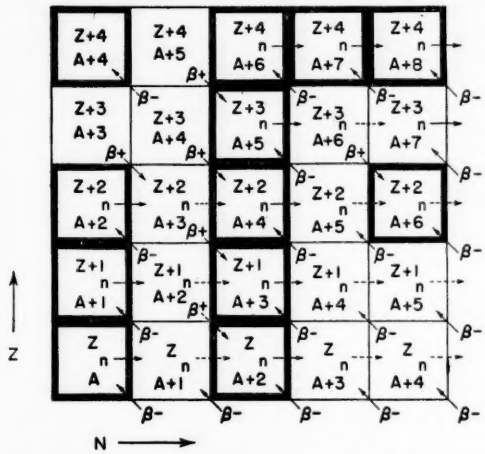

Fig. 6. A typical section of a nuclide chart showing beta stable nuclei outlined with heavy black borders.

unusually close to the valley of beta stability (forming the vertical ladder sequences in Fig. 4). Near the tops of the ladders the beta decay half-lives become relatively long and the equilibrium abundances are unusually large. These abundance peaks will be formed in the vicinity of mass numbers 80, 130 and 195, and it may be seen that there are abundance peaks at these positions in Fig. 5. These were first attributed to the effects of neutron capture on a fast time scale by CORYELL (1956).

If neutron capture on a fast time scale goes as far as mass number 287 before fission takes place, as the writer has suggested, then, after neutron capture stops, the abundance peak at mass number 287 will be destroyed by spontaneous fission. The fission fragments can be expected to peak in abundance near mass numbers 123 and 164 (CAMERON, 1957c). The first of these lies under the broad peak at mass number 130, but there is a secondary peak near mass number 164 in Fig. 5. BURBIDGE *et al.* (1957), attribute this last feature to stabilization effects associated with nuclear deformation in this region.

Further information can be obtained from an analysis of the abundances of nuclear isobars. Fig. 6 shows a typical section of a nuclide chart. Let us assume that the nuclide (Z, A) is a member of the slow time scale neutron capture path. Neutron capture leads to $(Z, A + 1)$ which usually has a beta decay half-life

short compared to the mean time between neutron captures. The beta decay daughter $(Z + 1, A + 1)$ then captures a neutron to form $(Z + 1, A + 2)$. This will usually decay almost entirely to $(Z + 2, A + 2)$. This latter nucleus will be called a "shielded isobar" because it is formed by neutron capture on a slow time scale but cannot be formed by neutron capture on a fast time scale. The fast time scale products of mass number $A + 2$ form the nuclide $(Z, A + 2)$ which will be called an "unshielded isobar". As further examples we may note that $(Z + 4, A + 6)$ is a shielded isobar and $(Z + 2, A + 6)$ is an unshielded isobar. The nuclide $(Z + 4, A + 4)$ cannot be formed by neutron capture but can be formed by proton capture or photo-disintegration on a fast time scale. It will be called an "excluded isobar".

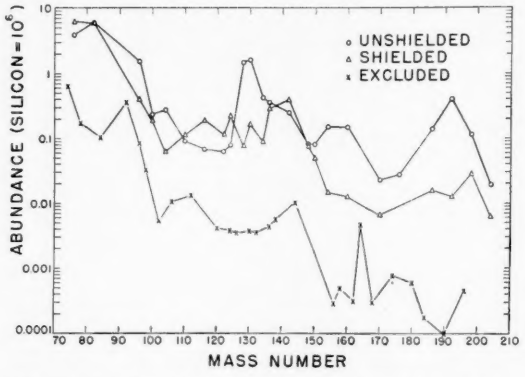

Fig. 7. The abundances of the three classes of isobars according to SUESS and UREY (1956).

The abundances of those isobars which can be unambiguously assigned to one of these three classes are shown in Fig. 7. The unshielded isobars, shown by circles, exhibit the behaviour expected from the preceding discussion. There are peaks at mass numbers 80, 130 and 195, consistent with formation by neutron capture on a fast time scale.

The closed shell peaks at mass numbers 90, 140 and 209 are too narrow to show up well in the abundances of the shielded isobars, shown as triangles in Fig. 7. However, there is one feature of neutron capture on a slow time scale which can be checked with this data. Note the general level of abundances near mass numbers 120 and 170. The ratio of abundances is approximately ten consistent with the capture of ten to twenty neutrons per initial silicon atom by heavier elements in a slow time scale process.

The abundances of the excluded isobars, shown as crosses in Fig. 7, follow the general trend of the shielded abundances but are lower by one to two orders of magnitude. This is the expected behaviour if the excluded isobars have been formed from the shielded nuclides by fast time scale processes. The abundances above mass number 150 are particularly interesting. There are four high points and six low points. The four nuclides with larger abundances can be formed by photodisintegration on both fast and slow time scales, whereas the nuclides with lower abundances can only be formed by photodisintegration on a fast time

scale. No such abundance fluctuations are apparent below mass number 150, and it is probable that those excluded isobars have been formed mainly by proton capture on a fast time scale.

A further check on the mechanism identifications that have been made can be obtained from an inspection of the odd-even abundance differences in Fig. 1. There is generally a factor of two to five between the neutron capture cross-sections of nuclides with odd and even mass numbers, and a corresponding difference between the equilibrium abundances, as can be seen from Fig. 2. The products of neutron capture on a fast time scale may or may not have a local smoothness, depending on the nature of the neutron termination. However, there are two effects which will certainly produce abundance regions with little or no odd-even effect. On the vertical ladder sequences of Fig. 4 every mass number contains a beta decay waiting point, and the half-lives of these beta decays should show a smooth progression up the ladder. Hence the broad peaks formed in the neutron capture on a fast time scale should show a reduced odd-even effect. It may be seen in Fig. 1 that this is so. Also the regions containing fission products resulting from spontaneous fission of very heavy nuclei should show a reduced odd-even effect if any substantial number of heavy nuclei have been subject to such fission. It may be seen in Fig. 1 that there is a reduced odd-even effect as mass numbers 123 and 164, which were suggested to be fission product regions resulting from the spontaneous fission of the mass number 287 region.

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NUCLEAR REACTIONS ON STELLAR SURFACES

The preceding discussion has given a fairly successful semi-quantitative account of the abundances of the elements heavier than boron and makes it reasonable to suppose that the natural abundances of these elements have been formed in stellar interiors. However, the theory does not contain any mechanisms for the production of deuterium and the isotopes of lithium, beryllium and boron, all of which are quickly destroyed in stellar interiors.

In this connexion it is instructive to consider the peculiar A magnetic variable stars. These stars contain general magnetic fields on the surface usually of some thousands of gauss and usually variable with a period of a few days. They have anomalous abundances of certain light elements and large overabundances of certain heavy elements, particularly in the rare earth region. The relative abundances of the heavy elements are inconsistent with formation processes in stellar interiors.

Two mechanisms have been suggested to account for these peculiar abundances (FOWLER *et al.*, 1955b; CAMERON, 1957c), both relying on variations in the strong surface magnetic field. In one mechanism it is postulated that a small part of the charged particles are accelerated by the magnetic field, and that the resulting energetic particles produce certain abundance anomalies by spallation reactions. In the other mechanism it is postulated that all of the charged particles are accelerated to form a high temperature plasma with a kinetic temperature of about 1 MeV, much as in certain proposed controlled thermonuclear reactors. Heavy elements are then synthesized in the plasma by the series of nuclear addition reactions involving protons and deuterons.

Peculiar A stars are not common enough in space to be able to produce the deuterium, lithium, beryllium and boron abundances by spallation reactions in

their surface layers. However, there are many other astrophysical situations which involve rapidly changing magnetic fields in stellar surfaces, and one or more of these may have made major contributions to the cosmic abundances of the light elements. These possible sources include the rapidly changing magnetic fields in supernova envelopes, any of the stars in which matter is being continuously ejected into space by surface magnetic activity, and the very numerous faint red dwarf stars which occasionally exhibit brilliant flares.

Recently HUNGER and KRON (1957) have observed the emission of polarized light from the T Tauri star NX Monocerotis. This star is one of a class of stars believed to be in the final stages of contraction from the interstellar medium. Polarized light is characteristic of synchrotron radiation from electrons moving in strong magnetic fields. Thus it seems likely that NX Monocerotis is still in the process of getting rid of its excess magnetic field and in slowing down its large angular velocity.

This suggests the very attractive possibility that nearly every star will modify the material cast away at the end of its initial contraction stage by accelerating particles and producing spallation reactions. Our sun may have done this and the material so processed may have been caught up in the gases from which the planets were formed. If this is the case the terrestrial abundances of deuterium, lithium, beryllium and boron may not be characteristic of the interstellar medium.

Note Added in Proof (August, 1958).

The writer has recently been investigating further the nuclear reactions likely to take place in supernova explosions. The following is a brief summary of the conclusions he has reached.

Because the central region of a star in an advanced stage of evolution is composed of a degenerate electron gas with a very high thermal conductivity, there is some doubt that the central temperature will ever rise high enough to trigger the iron-to-helium conversion process discussed above. If such a star has a mass in excess of the white dwarf limit of 1·25 solar masses, it would tend to contract until nuclear densities are reached (about 3×10^{14} g/cm^3). However when the central density becomes about 10^{11} g/cm^3, the Fermi energy of the degenerate electrons reaches the vicinity of 20 MeV. These electrons are then captured by the nuclei present; the capture proceeds until the capture products become unstable to neutron emission. In this way the nuclear charges are greatly reduced and the nuclei lose a large number of neutrons. When the nuclear charges become small enough, nuclear fusion occurs, and the resulting compound nuclei continue the neutron stripping process. Since most of the pressure at the centre of the star had been provided by the degenerate electrons which are removed by this iron-to-neutron conversion process, a rapid collapse of the stellar core is assured by this alternative mechanism.

Let us now consider conditions in the collapsing envelope. The local gravitational potential energy released during the collapse is approximately proportional to the cube root of the density attained; and as long as the gas is non-degenerate and the energy density of the radiation does not exceed that of the matter, the thermal energy of the matter increases adiabatically as the two-thirds power of the density attained. It follows that there is a limiting density at which the collapse will cease, when the thermal energy of the matter attains

the full value of the gravitational potential energy released. In a very massive and hot star it is likely that that region of the envelope which had been converted to carbon will stop collapsing when the density is about 10^5 g/cm^3 and the temperature is about 2×10^9 °K. There follows a series of nuclear reactions in which the carbon is converted mostly to oxygen and magnesium isotopes. Then another series of reactions takes over at a somewhat slower rate and converts the material into the isotopes in the region from silicon to calcium; the relative abundances of these isotopes in local equilibrium agrees quite well with the Suess–Urey abundance table. The energy released in these reactions is of the correct order of magnitude to blow off the supernova envelope.

The material, mostly of the iron abundance peak, which lay inside the carbon region will fall in until much higher temperatures and densities are attained. For this material, in an adiabatic compression, the energy content varies as ρ^n, where $1/3 < n < 2/3$, and hence the limiting density is much higher than for non-degenerate material. Very massive stars rotate very rapidly; hence for much of the material the collapse may cease when the rotational kinetic energy becomes equal to the gravitational potential energy released. Because of the enormously high thermal conductivity of the material, much of the energy released in the collapse of the inner portions of the core can be transferred to the outer portions, even on the explosion time scale of a few seconds. The outer parts of the core can then explode away from the star once the pressure of the envelope has been removed. In this way material forming the iron peak can be ejected into space.

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Meanwhile the inner core has been largely converted to a degenerate neutron gas. Its temperature will tend to lie in the region of 10^{11} °K. After all the core material has either been ejected or has fallen into the iron-to-neutron conversion region, the high thermal conductivity of the degenerate neutron gas will tend to transfer energy from the inner regions to the outer regions, sufficient to eject some of this material into space also. This will tend to be the case even more for less massive stars than for very massive ones, since the less massive stars have much less rotational kinetic energy and hence more material will tend to collapse rapidly into the neutron degenerate region. When this largely neutron gas is ejected into space, there will be many seed nuclei of intermediate atomic weight which can capture neutrons. Neutron capture on the fast time scale takes place until the neutrons have become exhausted.

Stars with masses very close to the white dwarf limit need not undergo supernova explosions at all. These stars would not tend to contract very rapidly, and hence it is likely that the internal temperature will at some point fall below the value required to maintain the helium-to-carbon conversion process in the star. However, when the boundary between the helium and carbon regions slowly collapses and attains a density of about 2×10^6 g/cm^3, a new phenomenon takes place. The nuclei are then squeezed so close together that their potential barriers become quite thin. Nuclear reaction rates then become much more sensitive to density than to temperature, and the reactions may be appropriately called pycnonuclear reactions (Gr. *pyknos*; compact, dense). Therefore, at this critical density the $^{12}C(\alpha,n)\ ^{16}O$ reaction commences again and rapidly heats the stellar interior until the gas becomes non-degenerate. This will generate a shock wave which will blow off a small part of the mass of the star. It will also tend to mix helium and carbon into the centre of the star. Thereafter,

every time the central density reaches about 2×10^6 g/cm^3, a further explosion follows until the mass of the star has been sufficiently reduced so that a stable white dwarf configuration can be formed with a central density less than the critical value. This mass will be about half a solar mass. GREENSTEIN (1957) has found that the white dwarf stars have an average mass of about 0·56 times that of the sun and an average central density of about 2×10^6 g/cm^3.

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SILICATE MELT SYSTEMS

By EDWIN ROEDDER

INTRODUCTION

MOST petrologists agree that the bulk of the rocks termed "igneous" have formed by the cooling of a hot, mobile mixture of earth materials called a "magma". There are considerable differences of opinion among these petrologists, however, as to further details of the processes of formation. For example, there is a school of thought holding that the magma from which some of the intrusive igneous rocks have formed, such as the large bodies of granite, was essentially a mass of solid crystals of various minerals, with merely a trace of liquid (or aqueous fluid) between the crystals. This liquid is considered to have been the cause of the apparent fluidity of the mass during movement into its present location, having acted both as a fluid "lubricant" for physical deformation of the mass and as a medium into which portions of crystals, more soluble as a result of being under pressure at their points of contact, dissolved and recrystallized elsewhere, thus relieving the stress. By continuation of this slow process, throughout the mass and for long periods of time, the "magma" eventually moved into an environment where the rate of heat loss to the surface exceeded the rate of heat gain from radioactivity within the mass,* or from heat flow from below, thus permitting the temperature of the mass to drop and the interstitial liquid to solidify.

Another school of thought would interpret these same granites as being the result of slow crystallization from a magma containing crystals and a sizable portion of what could best be termed a silicate melt, and in some cases a viscous but essentially crystal-free melt is envisaged as the starting magma. Although there is evidence in the form of glassy selvages, etc. that at least some magmas are essentially pure silicate melt (see SHAND, 1947, p. 6), and there is also adequate evidence that other "magmas" of similar bulk composition have had very little if any silicate melt present, it appears that the end results—the final solid rocks—do not differ greatly in mineralogy in these two extreme cases.

This merely illustrates the fact, pointed out by Eskola many years ago, that many natural systems approach a condition of phase equilibrium with respect to the particular temperature and pressure existing at the time. The true equilibrium assemblage at a given temperature will be identical, whether this state was approached by slow heating during metamorphism (and perhaps movement) of a thick sequence of sediments or by slow cooling during the solidification of a large intrusive body of liquid magma. The equilibrium referred to here deals only with the mineral phases present, and does not

* A completely insulated mass of rhyolitic magma of average, present-day composition will increase in temperature approximately 32°C every 10^6 years. The greater amount of radioactive elements present during the Precambrian would have caused this rate of evolution of heat to be significantly greater (55°C per 10^6 years at 2×10^9 years ago), under similar conditions at that time (ROEDDER, 1956).

concern the textural relations of the phases, except in so far as these textures aid or hinder the attainment of the equilibrium.* These textures may, however, reveal many details of the history of the rock, if they can be correctly interpreted.

Upon slow cooling from a state of equilibrium, the phase assemblage (including any liquid) continuously reacts to approach new equilibria, particularly if an appreciable amount of liquid phase is present through which these reactions may occur. In many rocks, however, a point is apparently reached where the drastic decrease in the rate at which reactions occur, with decrease in temperature, results in "freezing in" the assemblage present at that time. These are the materials with which the petrologist must work, attempting to reconstruct the thermal and compositional history of the rock from the available clues.

In this chapter the experimentally determined silicate melt systems of most interest to petrologists will be reviewed, but no attempt will be made to cover the entire broad field of silicate melt systems, and very little will be said concerning subsolidus equilibria. For a much more comprehensive survey, the reader is referred to the 1600 page treatise entitled *The Physical Chemistry of the Silicates* by EITEL (1954a) which includes almost all of the phase diagrams reproduced in this chapter and many others of lesser interest to petrologists. Most of the phase diagrams reproduced here will also be found in a very useful compilation of phase diagrams for ceramists, published by the American Ceramic Society (LEVIN *et al.*, 1956), which indicates the importance of these phase equilibrium studies to the various ceramic industries. This compilation also contains a four-page glossary of phase equilibrium terms (pp. 5–8); for the most part, the terminology in this chapter follows this usage.

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Reviews on the general subject of silicate melt systems as applied to petrology will also be found in several papers by BOWEN (1935b, 1937, 1954), MOREY (1936b, 1937, 1956) and SCHAIRER (1944, 1951, 1957), to whom the author is indebted for much of the material presented here. A classic book by Bowen, published thirty years ago (BOWEN, 1928), is still a standard reference for applications of melt systems to petrology.

Only "dry" (i.e. containing no readily volatile substances such as H_2O or CO_2) systems at near-atmospheric pressures (published up to 1957) will be discussed, inasmuch as the "wet" or "hydrothermal" systems have been covered quite adequately in Volume 1 of this series (ROY and TUTTLE, 1956), and silicate systems at high pressure constitute a subject by themselves. As most of the silicate systems discussed beyond have been studied at the Geophysical Laboratory of the Carnegie Institution of Washington, the reader is referred also to a convenient list of systems investigated at the Geophysical Laboratory (ADAMS, 1952). I want to express my appreciation for the help received from various members of the Geophysical Laboratory, and in particular from J. F. Schairer, who reviewed the manuscript and offered many helpful suggestions.

EQUIPMENT AND TECHNIQUES

As with many fields of science, progress in the study of silicate melt systems has been closely linked with progress in a number of experimental techniques. From the standpoint of experimental techniques, there are five steps in the determination of the phase diagram of a silicate system by the "quenching" method,

* Grain size is most important in this respect, although theoretically the surface areas involved will also influence the equilibrium itself.

as normally used at the Geophysical Laboratory: (1) synthesis, (2) homogenization, (3) equilibration, (4) quenching, and (5) identification.

1. *Synthesis*

The essential problem here is to weigh out appropriate amounts of suitable materials, to make the various desired compositions. This is not as simple as it appears, for although it is comparatively easy to obtain *pure* materials, relatively free from specific, stated impurities, it is very difficult to obtain materials of *stoicheiometric*, or at least precisely known, composition. Analytical reagents that might be used, such as the alkali carbonates, as normally supplied, bear analyses for trace amounts of various heavy metals, insolubles, etc. but seldom have specified the much larger amounts of H_2O or other diluents, which, although harmless in most analytical applications, do cause serious deviations from stoicheiometric composition.

Not only must the materials used be pure and of known composition, but they must have other desirable properties. For example, it has long been known that the alkalis are more or less volatile at elevated temperature. Losses from this cause are largest if CO_2 and H_2O are also being driven off from the mixture (KRACEK, 1932). For this and other reasons, it is necessary to prepare first a crystalline alkali silicate from the alkali carbonate and silica, and then weigh the calculated amounts of this material, if the alkalis are desired in the batch. It is also desirable, and in the case of viscous melts it is imperative, to use materials that will be relatively soluble during the homogenization, although this requires a compromise, in that the fine grained, readily soluble varieties of such materials as Al_2O_3 and MgO are also hygroscopic and apt to be far from stoicheiometric.

If the preparation of the batch is performed with due care, its composition, as determined by synthesis, will probably be closer to the desired composition than is possible to determine by chemical analysis of the completed batch.

2. *Homogenization*

The object of this step is to convert the mixture of weighed raw materials to a homogeneous glass, so that even tiny portions (a few milligrams) of the batch will be of the same gross composition as the entire batch. This homogenization usually consists of repeated fusion, quenching and crushing. A very sensitive test for homogeneity consists of observing some of the crushed glass embedded in a liquid exactly matching it in index of refraction, making use of the more rapid change of the index of refraction of the oil with change in temperature to obtain a perfect match. By this method extremely small, as well as very local, variations in the composition of the glass result in rather prominent index variations.

In many systems, particularly for subsolidus studies, sintering of the finely-ground batch is used as a method for both homogenization and equilibration.

3. *Equilibration*

The object here is to hold small amounts of the prepared glasses, and/or portions of them that have been crystallized previously, at a variety of constant, known, temperatures for lengths of time adequate to attain equilibrium. The technique for preparing the tiny charges, usually in platinum foil envelopes, was

first described by SHEPHERD *et al.* (1909); a number of experimental details are given by ROEDDER (1951a).

Two of the major problems in silicate phase equilibrium research lie in the words "constant, known, temperatures". The published information on high temperature furnaces and temperature controllers for such work is rather scattered (ADAMS, 1924; ROBERTS, 1925, 1941; FAUST, 1936; ROEDDER, 1952). An excellent controller, using a modification of the bridge method of ROBERTS (1925), has been designed by Mauer and later revised by Mauer and J. England. Although this controller has not been fully described in the literature, a few details of the construction and operation of some earlier versions are given in LEVIN and UGRINIC (1953), and BOGUE (1955, p. 311). In general, platinum-wound furnaces are used, designed to heat small diameter vertical ceramic tubes, in which the sample is hung. The normal construction involves a can of insulation (usually MgO) surrounding the furnace tubes, so that only a few hundred watts of electric power are consumed.

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In the measurement of high temperatures in silicate research, the e.m.f., measured potentiometrically (WHITE, 1941a), of thermocouples of pure platinum against a platinum alloy with 10 per cent rhodium are usually used, with the cold junction in crushed ice and water. As the e.m.f. of such thermocouples is rather small (10–12 μV/deg), considerable care must be used to isolate the thermocouple circuit from stray conducted or induced currents from the furnace heating circuit, and from stray thermal e.m.f.s (WHITE, 1941b). For most work the deviations of such thermocouples from the available tables of e.m.f. vs. temperature (for example, ADAMS, 1914), are large, even when they are newly made from the best available wire. Such thermocouples will also exhibit drift in their e.m.f., with use, due to annealing of the wire (ROESER and WENSEL, 1935), and particularly from contamination with iridium (DAY *et al.*, 1906, p. 286), alkalis (ROEDDER, 1951a, p. 90), or iron (BOWEN and SCHAIRER, 1932, p. 181). As a consequence, the thermocouples are usually calibrated, at frequent intervals, using as reference points the melting points of various pure materials. In the publications of the Geophysical Laboratory, these melting points are specified in terms of the temperature scale based on the nitrogen gas-thermometer calibration of DAY and SOSMAN (1911, 1912).

Representative fixed points on this scale are the melting points of zinc, 419·4°C; silver, 960·2°C; gold, 1062·6°C; synthetic diopside, 1391·5°C; palladium, 1549·5°C; and platinum, 1755°C. For convenience, certain secondary reference materials are sometimes used, such as pure NaCl, 800·4°C; synthetic $Li_2O \cdot SiO_2$, 1201°C; synthetic pseudowollastonite or $\alpha\, CaO \cdot SiO_2$, 1544°C; and synthetic anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$, 1550°C (ROBERTS, 1924). The use of specific points such as these has the advantage that regardless of the changes that have already taken place in the adopted high temperature scales (STIMSON, 1949; CORRUCCINI, 1949; and WILSON, 1953), or that may take place in the future, the temperatures reported in the work can be recalculated to the scale currently adopted. For consistency, the Geophysical Laboratory has used this "Geophysical Laboratory Scale" in all their publications since 1914.* A

* Temperatures on the diagrams beyond are given as presented in the original references, and hence are not strictly comparable in all cases. The differences between the various scales are not very significant except at temperatures over 1500°C, where the differences may be up to 20°C.

discussion of the interrelationships of the various temperature scales will be found in SOSMAN (1952).

The specific furnace technique used will vary with the nature of the problem. The normal quenching technique, with platinum resistance furnaces, was originally described by SHEPHERD *et al.* (1909), and later by FAUST (1936). Further details on the normal technique and some of the variations invoked for use with systems including FeO as a component have been described by BOWEN and SCHAIRER (1932), and by ROEDDER (1951a and 1952). Numerous other papers in the literature mention variations in the technique for other specific applications.

Considerably different techniques are used in special cases. The gradient furnace, wherein a long strip of the material under investigation is placed in a constant known thermal gradient, has been used as a quick reconnaissance method for determining the specific temperatures at which individual quench runs should be made (GRAUER and HAMILTON, 1950; TUCKER and JOY, 1957). The ribbon furnace, in which a small amount of the sample is placed on an electrically heated platinum ribbon and observed telescopically, is particularly useful for high temperature studies where quenching is difficult. Temperatures in such cases are usually read with an optical pyrometer focused on the strip. Many useful variations of this device have been described, including one designed for use on a microscope stage (ROBERTS and MOREY, 1930; KEITH and ROY, 1954, p. 6). For temperatures much above 1600°C, where the platinum or platinum–rhodium resistance element begins to vaporize too much for convenient use, a variety of other furnace types are used, including electrical resistance furnaces with heating elements made of carbon tubes, spirals or granules, rare earth rods, tungsten or molybdenum ribbon or wire, electric arcs, oxy-gas and oxy-hydrogen flames, and solar energy. These high temperature furnaces are used mostly for research in the oxide systems not including SiO_2, as the presence of SiO_2 in a system brings the temperatures down into the working range of the platinum resistor in most cases.

The largest single problem, present in all silicate research, is that of establishing and verifying the existence of equilibrium in any given experiment. The methods used to verify equilibrium will be controlled by the nature of the phase assemblage, and the specific methods used for one type of assemblage, such as the metal systems (BREWER, 1950) are not necessarily applicable to another type, such as the silicate systems.

In silicate phase research, there are a number of criteria *indicating* that equilibrium has been established. Some of these, such as uniformity of distribution of phases and the absence of rounded or corroded crystals, are helpful criteria, but are not reliable. Lack of further change when held at the same temperature for a longer time is a necessary but not positive criterion. The existence of metastable equilibrium, even for long periods of time at high temperatures, is particularly common in the silicates and may be practically impossible to avoid. Thus in the system K_2O–MgO–SiO_2 ROEDDER (1951a) was unable, even with long runs, to establish equilibrium at the liquidus with the "correct" modification of silica (quartz), known from the system K_2O–SiO_2 (KRACEK *et al.*, 1929, p. 1860), and from other systems, to be the stable modification at such temperatures.

Another very valuable "proof" of equilibrium, at least with respect to a metastable process, if not the stable process, is that of duplication of results

by starting with the same composition in a different physical state (e.g. crystalline and glassy). Thus, if a glass made of components A, B and C, and a mixture of crystals of A, B and C (of the same gross composition), when heated to a given temperature, both yield crystals of B, crystals of C and liquid, one can be reasonably sure that crystals of A are *not* stable (they melted) and that the assemblage B, C and liquid represents at least metastable equilibrium. It does *not* tell us, however, that some other polymorphic form of B, or C (or even A), is not a truly stable phase under these conditions, or that some binary or ternary compound of A, B and C is not stable. For example, the binary system $K_2O \cdot SiO_2$–SiO_2 as deduced from a study of the ternary system H_2O–K_2SiO_3–SiO_2 (MOREY and FENNER, 1917) exhibited only one intermediate compound, $K_2O \cdot 2SiO_2$, and showed a eutectic between this compound and SiO_2 at 525°C, at a K_2O/SiO_2 ratio of 1/4. This eutectic was later shown to be metastable, however (KRACEK *et al.*, 1929); if enough time is permitted, a new stable phase, coincidently of composition $K_2O \cdot 4SiO_2$, will appear. This compound is exceedingly slow to nucleate and grow in these viscous liquids. Where formerly there had been a deep, low-temperature (metastable) eutectic "valley" on the diagram, there is now a stable compound with a considerably higher melting point than the metastable eutectic (see Fig. 4).

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For such reasons as this, it is important to obtain as many different phases as possible in the precrystallization of the batches, to use as "seeds" in the equilibration runs, so that the reluctance of the system to initiate the formation of a new phase—the major cause of metastability—may be avoided. When nucleation is very difficult in the precrystallization, it is sometimes desirable to subject the samples to a mild "hydrothermal" treatment to induce crystallization. One such method involves sealing the sample, in a loose capsule, in an evacuated tube, along with another capsule containing a small amount of a natural water-bearing glass, such as obsidian (GREIG and BARTH, 1938, p. 98). At the temperature of the crystallization this yields a small water vapour pressure in the tube which increases the rate of nucleation and growth of crystals in the sample many orders of magnitude. With this technique one must be careful not to grow crystals so large that equilibration, by melting of the crystals, will be slow. In general, crystal size should be kept under 20 μ. If only a very small percentage of tiny crystals is formed in this manner, their behaviour can give a sensitive indication of the equilibrium even in exceedingly viscous glasses; thus if they grow slightly at one temperature, and become corroded at a higher temperature, the melting point of the crystals must lie between (GREIG and BARTH, 1938, p. 97). Ordinarily, if viscosities are low, nucleation is fast and seeding is not necessary. In some cases it appears that the transformation of an early-formed disordered to an ordered phase is the rate-limiting step in the attainment of equilibrium, as in the aluminium-silicon ordering in the feldspars (GOLDSMITH, 1953).

There is one further check on the existence of equilibrium, in the form of agreement of the data on a given point with data from nearby points. This is a powerful tool to detect disequilibrium. Unfortunately, however, *no* method of experimental or theoretical determination of phase relationships in a heterogeneous system can completely exclude the possible existence of other, more stable phases. Metastable phase diagrams can appear perfectly normal in all respects, and unless the possibility of the existence of other modifications or compounds can be deduced from crystal chemical considerations or from the

occurrence of such phases in other systems, or in nature, the diagrams will appear to represent true equilibrium conditions. Phases have been found in nature that do not show up on the appropriate silicate melt systems; some of these phases are apparently monotropic, and have no stability field, and others apparently form and are stable only under high pressures. In a few cases, however, it is apparent that the reactions forming them (usually in the solid state) have activation energies which are prohibitive of laboratory synthesis, but are permissive if geological time is available.

4. *Quenching*

The purpose of quenching is to bring the sample from the high temperatures, at which it was equilibrated, down to room temperature at such a rate that phase changes do not occur. The main reason for this is that it is generally inconvenient or even impossible to identify the phases present while the temperature is high. Quenching is done in a variety of ways, depending upon the ease with which the particular phase changes involved may occur. Highly viscous silicate melts may be cooled in air without fear of crystallization, as some of these take months or even years to crystallize even at optimum temperatures. On the other hand, liquids of low viscosity may crystallize, at least partly, even in the few tenths of a second during which they cool when suddenly submerged in cool mercury (as by the use of a platinum weight as a sinker, ROEDDER, 1952, p. 442), and of course the "snap" inversions in some crystalline phases will occur regardless of the cooling rate.

One problem developed in quenching is that of recognizing phases "formed on quench" from those present in the equilibrated batch at the furnace temperature. In some cases a few feathery, dendritic spines form on quench at the corners of the large solid euhedral crystals present at equilibrium. In other cases all liquid present in the charge in the furnace crystallizes on quench to a fine feathery mass, in which are embedded the large solid euhedral crystals that were present at the temperature of the furnace. If this sort of ambiguity cannot be eliminated by the obvious procedure of faster quenching, then it is quite possible that one of the other methods of recognition of phase change, such as differential thermal analysis (DTA), or heating or cooling curves (MOREY, 1923; 1936a, p. 1–3), might be used to advantage. Most silicates crystallize so sluggishly, however, and with such small heats of crystallization, that these dynamic methods are not very applicable (KRACEK, 1951).

5. *Identification**

The identification of the phases present and the determination of their composition is sometimes one of the most difficult aspects of phase equilibrium studies. As any of the characteristic properties of a phase may be measured to prove its existence or to discern a phase change (BREWER, 1950), recent developments in instrumentation, and a wider use of older techniques, have done much to aid phase identification.

Although in general a combination of thermal, X-ray and microscopic data is used to determine the composition and interrelationships of phases, the petrographic microscope is still the most useful tool in silicate studies, even when the

* This section is taken, with some modification, almost directly from CHRISTENSEN and ROEDDER (1952).

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optical properties of the phases are unknown at the start of the investigation. Petrographic methods are particularly useful with the quenching technique, as the quantity of sample required for a complete optical determination is very small. As many as seven distinct optical properties, any one or combination of which may be definitive of a phase, may, if necessary, be measured on a single crystal grain less than 10 μ in diameter (i.e. down to 0·001 μg) without destroying the grain. In the system pseudowollastonite–akermanite–gehlenite, for example, OSBORN and SCHAIRER (1941) used the interference colour of the melilite solid solution to establish its composition between akermanite and gehlenite, and hence determine conjugation lines and crystallization curves in the large solid solution field. It is far more convenient, however, to use different portions of the sample for each such determination, and hence 1 mg or more of sample is desirable. As most of the procedures used in the quenching technique provide samples of approximately 10 mg, there is adequate material left for other techniques such as the X-ray diffraction.

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Determination of the amount and composition of liquid present at high temperatures (or glass, its quenched equivalent) has been a considerable problem in many silicate systems, as glass does not have many of the properties so characteristic of crystalline solids. Centrifuging at high temperatures to separate liquid from crystals works rather well, as an adaptation of the well-known "wet-rest" method used so frequently in soluble salt–water systems at lower temperatures, but experimentally this method presents serious problems at high temperatures (see BIRCH, 1955; DERGE and SHEGOG, 1955; BOGUE, 1955). Heat-of-solution calorimetry has been used to determine the amount of liquid (glass) present in Portland cement clinker, in consequence of the differences in heat of solution of crystals and that of the glass (LERCH and BROWNMILLER, 1937), but this requires a knowledge of the latent heat of crystallization of all possible glass compositions in the system. A less elegant but exceedingly simple and convenient procedure involves the use of a porous relatively nonreactive material (e.g. sintered Al_2O_3), to remove the liquid from the batch by capillarity. The determination of the approximate amount of liquid present by the "quenching" technique is usually based on microscopic examination for glass in the quenched product. A more accurate method is available, however, when the index of refraction of the glass in the mixture of glass plus crystals can be obtained. If one knows the total composition of the mixture (by synthesis) and the composition of the crystal phase present (from petrographic examination), by the use of a previously determined plot of composition versus index of refraction for glasses in the system, one can determine both the composition of the glass and the relative amounts of crystals and glass present in the quenched sample. In silicate systems these determinations of amounts of liquid and crystal phases are usually used only as a guide to further work, and seldom as data on which to base an equilibrium diagram. For the determination of the temperature of eutectic points by observing the start of melting of all-crystalline material, microscopic examination for the presence of glass is not so sensitive a test sometimes as is the sintering of the powdered crystalline material.

Next to the petrographic microscope, the most useful tool in the identification of the phases in silicate work is the diffraction of X-rays. X-ray techniques are not a panacea, however, and some of the limitations have been discussed by BREWER (1950). Because of the minute percentage of crystalline phase

present, such techniques are useless for determining the crystal phase at the liquidus unless such crystals can be determined by petrographic methods to be identical with other crystals occurring in larger amounts in samples equilibrated at lower temperatures. Of particular significance is the limitation of X-ray techniques in systems involving solid solution series between "end members" whose unit cells are practically identical in size and shape.

One very important technique, which should have even greater application in the future, is the use of the high temperature X-ray camera for identification of the phases present while the sample is still in the furnace. Although experimentally difficult, this technique has the great advantage of being a direct method, and thus avoiding ambiguity resulting from crystallization or rapid inversions on quench. Many designs of high temperature X-ray cameras are described in the literature, but most of these are made for detecting phase changes in single crystals or powdered solids (for example, BASSETT and LAPHAM, 1957), and hence are not readily applicable to solid–liquid equilibria.

Method of Presentation of Data

The phase rule of Willard Gibbs, stated simply, is that for a system in equilibrium, the number of degrees of freedom must equal the sum of the number of components, plus two, minus the number of phases. The degrees of freedom are taken in the definition of MACDOUGALL (1939, p. 136): "The number of *intensive* variables which can be altered independently and arbitrarily (within certain limits) without bringing about the disappearance of a phase or the formation of a new phase is called (in the thermodynamic sense) *the number of degrees of freedom* of a system." (Another widely-quoted definition of degrees of freedom involving the number of variables "which must be arbitrarily fixed in order to define the system", results in serious ambiguity and should be avoided.) A phase diagram is merely a graphical expression of the limits to which these variables can be independently and arbitrarily altered. As such it is usually a plot of one variable against another, with the limits indicated for given phase assemblages. In the diagrams presented beyond, pressure is not considered as a variable.

In unary (single-component) systems, the convention is to plot T as abscissa and P (vapour pressure or total pressure on the system) as ordinate.

In binary (two-component) systems, the convention in condensed systems is to plot composition as the abscissa (usually in weight per cent but occasionally mole per cent) against T as the ordinate. Most silicate melt systems can be considered to be condensed systems, in that the vapour pressures of the phases involved are negligible, and so no vapour phase appears and the effect of 1 atm external pressure is nil. An exception to this will be found in the systems bearing FeO. Here a variation from an essentially zero partial pressure of oxygen (as with a flow of carefully purified nitrogen) to even a small part of the 0·2 atm partial pressure of oxygen in air can change the phase assemblage drastically. In many cases such systems, although they are usually considered as "condensed" systems, are actually determined under some fixed, very low, but significant partial pressure of oxygen, such as that determined by the efficiency of the oxygen-removing train used to purify the nitrogen atmosphere.

In ternary (three-component) systems, the convention is to plot two compositional variables (per cent A and per cent B, per cent C being implicit in the

statement of the other two) on an equilateral triangle, and represent the temperatures of a given surface, such as the liquidus, by contours (isotherms) representing the height above the base of a three-dimensional triangular prism figure. The figure is projected onto the base along the temperature axis, as only two variables can be rigorously plotted on a two-dimensional diagram, and the compositions are most important.

One of the fortunate aspects of this type of plot, which is seldom used to the extent that it might be, lies in the fact that these diagrams can be used to determine *quantitatively* the amount and composition of each phase present, for any

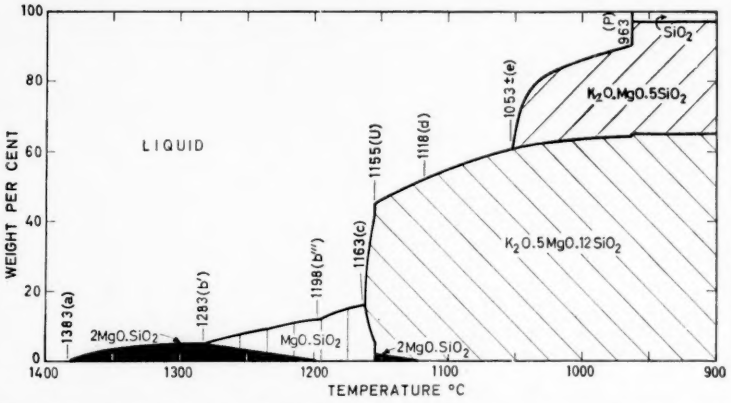

Fig. 1. Diagram showing the phases present, at equilibrium, in a mixture of composition "a", (Fig. 26) between liquidus and solidus, in the system K_2O–MgO–SiO_2. The temperatures of phase changes were obtained experimentally; the percentages were obtained by scaling Fig. 26. Letters in parentheses refer to points on Fig. 26 and Table 1. (After ROEDDER, 1951a, p. 227.)

composition in the system at any temperature. The methods for such operations are given, rather cursorily, in most phase rule texts. A short but rather lucid review of the principles will be found in LEVIN *et al.* (1956, pp. 9–29). Although graphical methods are customarily used in working with these diagrams, rigorous analytical methods have been described (MOREY, 1930). Quantitative information obtained by such methods reveals that some compositions have surprisingly abrupt changes in the total quantity of the various phases present during their cooling (or heating) history. These abrupt changes can usually be seen in a qualitative way, of course, by simple inspection of the diagram, but their rapidity and magnitude become much more apparent when a plot is made of the amounts of the various phases present in per cent of the total, vs. the temperature. Figure 1 is an example of such a plot, made from the graphically determined data of Table 1, showing the change in phase assemblage with temperature for a certain composition in the system K_2O–MgO–SiO_2 (Fig. 26). This composition shows, incidentally, one type of recurrent crystallization of forsterite, $2MgO \cdot SiO_2$. This means that forsterite is stable in two different temperature ranges, separated by a temperature range in which it cannot exist as a stable phase. Other compositions near to point "a", in the triangle $SV'''V'$ of Fig. 26, have *three* separate stability ranges for forsterite (see ROEDDER, 1951a, pp. 228 and 243).

Table 1. Phase Changes Occurring between the Liquidus and Solidus for a Mixture of Composition "a", Fig. 26
(See text and Fig. 1)

	Temperature (°C)	Phases present at equilibrium	Composition of the liquid lies—	Composition of the solid lies—	Weight per cent					
					Liquid	$2MgO \cdot SiO_2$	$MgO \cdot SiO_2$	$K_2O \cdot 5MgO \cdot 12SiO_2$	$K_2O \cdot MgO \cdot 5SiO_2$	SiO_2
1.	> 1383	All liquid	at *a*	none present	100	0				
	at 1383		at *a*	at *L*	100	0 +				
	1383–1283	Forsterite + liquid	along *a–b′*	at *L*	100–95	0–5	0			
	at 1283		at *b′*	at *L*	95	5	0 +			
	1283–1198	Forsterite + protoenstatite + liquid	along *b′b‴*	along *LK*	95–88	5–0	0–12			
	at 1198		at *b‴*	at *K*	88	0 +	12			
	1198–1163	Protoenstatite + liquid	along *b‴ –c*	at *K*	88–84	0	12–16	0		
	at 1163		at *c*	at *K*	84	0	16	0 +		
	1163–1155	Proto. + $K_2O \cdot 5MgO \cdot 12SiO_2$ + liquid	along *cU*	along *Ku*	84–58	0	16–4	0–38		
	at 1155		at *U*	along *uu′*	58–55	0–2	4–0	38–43		
	1155–1118	Forst. + $K_2O \cdot 5MgO \cdot 12SiO_2$ + liquid	along *Ud*	along *u′S*	55–47	2–0	0	43–53		
	at 1118		at *d*	at *S*	47	0 +		53		
	1118–1053±	$K_2O \cdot 5MgO \cdot 12SiO_2$ + liquid	along *de*	at *S*	47–40	0		53–60	0	
	at 1053±		at *e*	at *S*	40			60	0 +	
2.	1053±–963	$K_2O \cdot 5MgO \cdot 12SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$ + liquid	along *eP*	along *Sp′*	40–10			60–64	0–26	0
	at 963		at *P*	along *p′a*	10–0			64–65	26–32	0–3
	< 963	$K_2O \cdot 5MgO \cdot 12SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$ + Tridymite (no liquid)	none present	at *a*	0			65	32	3

1. Experimentally determined points—for data see Preparation 49 in Tables 1–5 of ROEDDER, 1951.
2. Not determined directly on this composition due to the large percentage of crystals present causing experimental difficulties. Data obtained from other points in the diagram.

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Table 2. Phase Changes Occurring between the Liquidus and Solidus for a Mixture of Composition "a", Fig. 10
(See text and Fig. 2)

Temperature (°C)	Phases present at equilibrium	Weight per cent					
		Liquid	CaO	$3CaO \cdot SiO_2$	$3CaO \cdot Al_2O_3$	$2CaO \cdot SiO_2$	$5CaO \cdot 3Al_2O_3$
> 1600	All liquid	100	0				
at 1600		100	0 +				
1600–1500	CaO + liquid	100–95	0–5	0			
at 1500		95	5	0 +			
1500–1470	CaO + $3CaO \cdot SiO_2$ + liquid	95–92	5	0–3	0		
at 1470		92–58	5–0	3–13	0–29		
1470–1455	$3CaO \cdot SiO_2$ + $3CaO \cdot Al_2O_3$ + liquid	58–43	0	13–15	29–42	0	
at 1455		43–12		15–0	42–69	0–19	
1455–1335	$3CaO \cdot Al_2O_3$ + $2CaO \cdot SiO_2$ + liquid	12–5		0	69–74	19–21	0
at 1335	($2CaO \cdot SiO_2$ inverts at 1420°)	5–0			74	21–22	0–4
< 1335	$3CaO \cdot Al_2O_3$ + $2CaO \cdot SiO_2$ + $5CaO \cdot 3Al_2O_3$	0			74	22	4

Another similar plot is shown in Fig. 2, made from the data of Table 2, for a composition "a" in the system CaO–Al_2O_3–SiO_2 (Fig. 10). Obviously there will be abrupt breaks in the amounts of phases present while the particular composition chosen goes through invariant points (points *c* and *e* for Fig. 1, and points *A* and *B* for Fig. 2), but the tremendous changes in the phase composition of these examples with very minor drops in temperature, particularly Fig. 2, are noteworthy. They are strictly a result of the geometric relations of the gross composition of the batch to the pertinent boundary curves, and their corresponding Alkemade lines, but crystallization paths such as these must

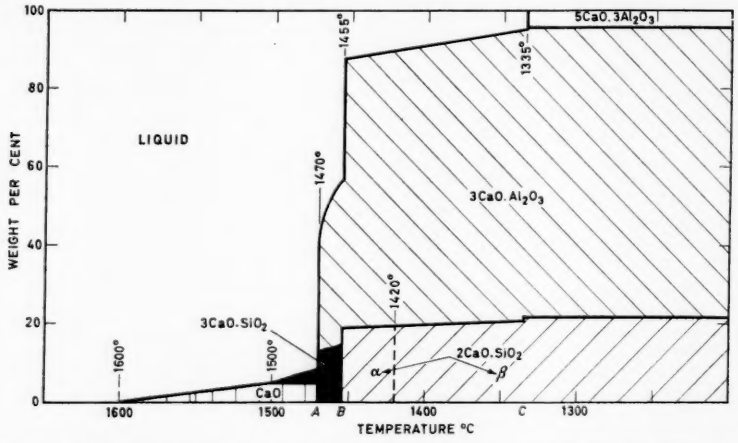

Fig. 2. Diagram showing the phases present at equilibrium in a mixture of composition "a" (Fig. 10), between liquidus and solidus, in the system CaO–Al_2O_3–SiO_2. The data, obtained by scaling an enlarged copy of Fig. 10, are given in Table 2.

certainly have their counterparts in the multicomponent systems representing rock magmas. It is difficult, in fact, to visualize such a complex system where there will *not* be rather abrupt changes in the amounts, and ratios, of the crystallizing phases on cooling.

Another possible method of representation of the data of a ternary system such as K_2O–MgO–SiO_2 would involve for example tracing the changes in composition, and temperature, of the system MgO–SiO_2, with small additions of K_2O. This is, in effect, viewing from the K_2O corner a series of non-binary sections through the diagram, each at constant K_2O content. This is illustrated in Fig. 3 (see also KRACEK, 1939, p. 2873). A variant of this was used by MOREY (1932), in which he showed on a composition plot the lateral displacement of boundary curves in the system Na_2O–CaO–SiO_2 with additions of B_2O_3, by superimposing the new boundary curves for 1 per cent and 5 per cent added B_2O_3 on those for the pure system. A variety of other methods have been developed for representing ternary systems, but these are not as generally convenient as the usual equilateral composition plot.

In some instances a four-component system, containing only small amounts of one of the four components, is represented simply as a three-component system, with a plot or merely a statement of the amount of the fourth component.

Examples of this are common in systems containing FeO as a component; these, even though run in a pure nitrogen atmosphere, in containers of pure iron, always contain small, equilibrium amounts of ferric iron. This is really another component, but as its concentration is insufficient to form significant amounts of independent ferric iron phases, the system is presented as though it contained one less component, and lines are drawn to show the Fe_2O_3 content in the various compositions, under some specified conditions (see Fig. 15).

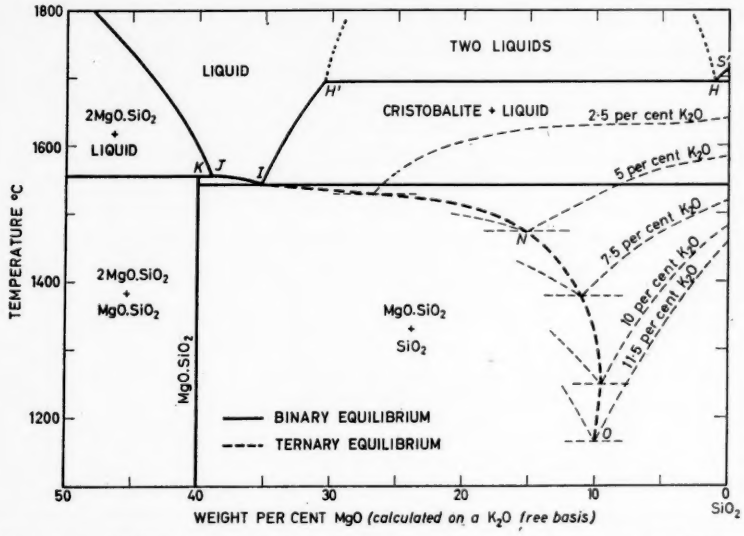

Fig. 3. Equilibrium diagram of the system MgO–SiO_2, after BOWEN and ANDERSEN, and GREIG (solid lines), showing the effects of various additions of K_2O on the $MgO \cdot SiO_2$–SiO_2 eutectic I, as recalculated from the system K_2O–MgO–SiO_2 (broken lines). The letters refer to points on Fig. 25

One very useful type of diagram, particularly for complex ternary systems, is the isothermal section. This is in effect a plane through the triangular prism model of the system, and shows the phase assemblage for any composition, at the specified temperature. On it can be represented the tie lines connecting the compositions of coexisting phases, for example solid solutions and liquid solutions; this information cannot be represented rigorously on the general (non-isothermal) ternary diagram, as there will be an infinite array of such lines. The isothermal section has long been used by the chemists to represent the phase relations in ternary systems including two salts and water, as this type of diagram is particularly suited to represent the data which, for convenience in the laboratory work, are usually obtained under isothermal conditions. A simple example is given in Fig. 31, showing an isothermal section through the system Na_2O–Fe_2O_3–SiO_2 at 825°C (BOWEN *et al.*, 1930). This figure shows areas representing four types of equilibria in the condensed system: trivariant (liquid only); divariant (one crystal phase and liquid, joined by radial tie lines); monovariant (two crystal phases and a coexisting liquid, making a "three-phase triangle"); and invariant (three crystal phases and liquid). The three-phase

triangles in a simple system such as Na_2O–Fe_2O_3–SiO_2 can be drawn by inspection of the liquidus phase diagram (Fig. 30). In a system involving solid solutions, however, the three-phase triangles must be established by experimental measurements of the compositions of coexisting phases. As there are infinite numbers of such three-phase triangles in any system involving solid solutions, it is conventional to represent only a few of them on the diagram, either as triangles or as tie lines connecting two coexisting phases, to illustrate their general shape and direction (see, for example, Fig. 47).

In quaternary (four-component) systems, the problems of representation of the data become severe, as three dimensions are needed to represent composition alone, unless simplifying restrictions are made, or "line-symbols" are used in place of points for the representation of compositions, (REIMERS, 1946; DOLAR-MANTUANI, 1957). Thus a three-dimensional model (usually a regular tetrahedron) is needed to represent the compositions, and the other variable, temperature, can only be represented by spot figures, written in on the solid model. As three dimensions are needed to represent unambiguously the three independent compositional variables, any attempt to represent a quaternary system on a two-dimensional sheet of paper must, of necessity, be far from rigorous.

A number of different techniques are used to reduce quaternary phase diagrams to two-dimensional drawings. If the system is simple, a perspective drawing of an apparently transparent model showing the univariant boundary lines can be made, or a plan view of the four limiting ternary systems comprising the four sides of the tetrahedron is shown, folding down three of the sides to the plane of the paper on which the fourth sits. In other examples, a transparent tetrahedron is drawn, with cross-cutting triangular planes representing the ternary subsystems that separate the diagram into smaller individual quaternary subsystems (Fig. 58).

The most satisfactory method of representing the phase equilibria within a quaternary system is the use of a series of sections through the system. In most cases these constitute ternary, or at least partially ternary, sections joining the composition points of three compounds or components (for example, see Fig. 53). Although these diagrams may appear as normal ternary systems, they frequently contain portions representing non-ternary (quaternary) equilibrium, and cannot be "read" in the usual fashion (for example, see Fig. 41, and discussion in SCHAIRER, 1942). Thus, where four-phase univariant lines in the quaternary system, representing equilibria between a liquid and three solids, are cut by any arbitrary triangular planes, the points appear as ternary invariant points; to distinguish them Schairer has given them the name "piercing points" (SCHAIRER, 1942, p. 253). If the compositions of all four phases at the point may be expressed in terms of the three compositions at the apices of the triangle, then the point *is* a true ternary invariant point, and the section, or at least this part of it, represents a ternary subsystem. In some quaternary systems, where there are no convenient ternary sections to be drawn, a series of sections at different fixed percentages of one component are used to illustrate the equilibria within the tetrahedron.

One further graphical method for representing quaternary equilibria in two dimensions deserves mention. This has come to be known as a "Schairer diagram," as it is a procedure first described by SCHAIRER (1942) for representing

the univariant lines (three solid phases and liquid) within a quaternary. It shows their relationships to the quaternary invariant points, and to the ternary invariant points on the four limiting ternary faces of the tetrahedron as well as on ternary subsystems within the quaternary. An example of the use of this device for illustrating equilibria in the system K_2O–MgO–Al_2O_3–SiO_2 is shown in Fig. 59. The phases coexisting in equilibrium are indicated, the direction of drop in temperature on univariant lines is apparent, and spot temperatures can be written in at invariant points.

SILICATE MELT SYSTEMS OF PETROLOGICAL IMPORTANCE

Scope

In a review of this length, it is obvious that only a few of the many hundreds of diagrams may be presented and discussed. LEVIN *et al.* (1956), list over 800 diagrams of interest to ceramists, and the bulk of these contain silica and are of interest to petrologists.

The following discussion will hence be limited essentially to diagrams in the eight-component "system" K_2O–Na_2O–CaO–FeO–MgO–Fe_2O_3–Al_2O_3–SiO_2. This "system" has been chosen as it represents, in only eight components, a reasonably close approach to the composition of most ordinary igneous rocks.

Table 3. Average Composition of Igneous Rocks
(from CLARKE, 1924, p. 29)

SiO_2	59·14
Al_2O_3	15·34
Fe_2O_3	3·08
FeO	3·80
MgO	3·49
CaO	5·08
Na_2O	3·84
K_2O	3·13
H_2O	1·15
TiO_2	1·05
ZrO_2	0·039
CO_2	0·101
Cl	0·048
F	0·030
S	0·052
P_2O_5	0·299
MnO	0·124
BaO	0·055
	99·848

Table 3 lists CLARKE's (1924) data for the average composition of igneous rocks as sampled from the crust of the earth. From this table it will be seen that over 99 per cent of the average igneous rock consists of the top ten oxides, and the top eight make up nearly 97 per cent. TiO_2 and all the constituents below it on the table will be omitted in the following discussion as they are present in small amounts and have comparatively little effect on the bulk phase assemblage obtained. H_2O is different, however. Although it is merely another component,

in the strict sense, it raises special experimental problems, and has considerable effect on the bulk phase assemblage. As systems involving H_2O have been discussed in the first volume of this series (ROY and TUTTLE, 1956), they will be omitted here, but it should be remembered that H_2O is present in significant amounts in most, if not all, magmas. The diagrams presented beyond will be affected by this extra component in several qualitatively predictable ways. Although some of the hydrous minerals that might form under these conditions, such as certain amphiboles, can be considered to approximate the hydrous equivalents of well-known anhydrous phases, there are other hydrous phases, such as muscovite, for which there are no single anhydrous equivalents. In this latter case, the presence or absence of H_2O may have rather drastic effects on the phase diagrams. In addition to causing the formation of new phases, the presence of even a small amount of water will cause a considerable lowering of the liquidus (and solidus), as well as a drastic lowering of the viscosity, of most silicate melts. These effects are readily explained, mechanistically, in the breaking of Si–O bonds by the entrance of hydrogen ions. As a consequence, anhydrous phases that are not stable at the temperatures of the liquidus in the anhydrous system, may crystallize from the liquid phase where the liquidus has been lowered sufficiently, and the lowered viscosity results in easier diffusion and nucleation, as well as more rapid flow under a given pressure differential.

There have been no direct studies of equilibria in this eight-component system. Although it would be experimentally simple to add all eight components to a given batch, identification of the phases obtained (particularly the solid solutions), would be exceedingly difficult, and there would still be the problem of representation. Just to represent the composition variables alone, with no dimension for representing the temperature variable, would require a diagram drawn in seven dimensions. Obviously, limiting assumptions must be made, to simplify the system to a manageable number of variables, and the work of the Geophysical Laboratory since its inception in 1907, and of many other laboratories studying phase equilibria of interest to petrology, has been along these lines. The approach has been to start with simple binary systems between individual pairs of these components, followed by the ternary systems, then the quaternary systems, etc. Although there are fifty-six possible ternary combinations and seventy possible quaternary combinations in an eight-component system, not all of these need be determined. This is fortunate, in that up to the present time, not even one single quaternary silicate system has been completely determined. As the work is aimed at the elucidation of rocks, simplifying assumptions may be made based on the composition of rocks. Thus, as silica is present in practically all rocks, systems not including silica need not be considered essential. They cannot be ignored, in that the phases formed in these systems may occur also in the systems with silica, and they represent limiting cases for the equilibria involving silica, but as most rocks contain forty or more per cent silica, these considerations are not very important. Other possible compositional limitations that may be assumed, in order to simplify the system, stem from the fact that igneous rocks, although containing significant amounts of all eight of the oxides mentioned, usually contain at least some of these in amounts corresponding to simple ratios. This is merely a logical consequence of the fact that rocks are made of a comparatively few minerals, but it does make it possible to represent the petrologically important

portions of relatively complex systems with far fewer components. Thus a saturated basalt, the bulk composition of which can be reasonably approximated by the six-component system CaO–MgO–FeO–Na_2O–Al_2O_3–SiO_2, can also be represented, with little loss in rigour, by the four-component system diopside ($CaO \cdot MgO \cdot 2SiO_2$)–ferrosilite ($FeO \cdot SiO_2$)–albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$)–anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$). Still further simplification lies in the similarity with which certain pairs of elements behave. Thus small amounts of ferrous iron can be lumped with magnesium, with comparatively little stretching of the facts. In actual practice, there has been sufficient study of the relative behaviour of Mg^{++} and Fe^{++} in silicate melts, that the concentration of iron relative to magnesium in the residual liquids from the basalt "system" above can be predicted, qualitatively, with a fair degree of certainty. Thus the basalt "system" diopside–ferrosilite–albite–anorthite can be further simplified, with additional but still minor losses in accuracy, by the ternary system diopside–albite–anorthite.

This type of simplification is necessary if the complex natural systems are to be placed on a rational basis. The simplifying assumptions made would be very hazardous, however, were it not for the fact that the results of the more complex systems—the rocks themselves—are always at hand, and provide a framework of facts and observations, obtained by the study of rocks in the field and in the laboratory, into which the experimental work must fit. When contradictions occur, further work in the field, or in the laboratory, is needed. By this process, in which each discipline nicely supplements the other, we may hope to obtain an understanding of the processes whereby rocks have formed in nature.

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Specific Systems in the More General System K_2O–Na_2O–CaO–FeO–MgO–Fe_2O_3–Al_2O_3–SiO_2

For a *complete* understanding of any complex system, all limiting simpler systems should be determined first. In order to limit the presentation to those diagrams of most direct interest to petrology, however, only systems with SiO_2 will be given here, and although the subsolidus relations are of great importance to petrology, space prevents their being covered. A number of other possible systems, involving only oxides other than SiO_2, have been determined and are given by LEVIN *et al.* (1956). In the diagrams which follow, it is particularly instructive to observe in each the composition and temperature of the last residual liquids to solidify. If ferrous iron is present, it will become concentrated in the residual liquids under equilibrium or disequilibrium crystallization, unless the alkalis and alumina are also present. In this case, the residual liquids, without exception, are seen to approach a composition corresponding to quartz plus alkali feldspar. The liquidus temperatures for such residual mixtures are very low unless no ferrous iron, or alkalis plus alumina, are present.

Actually, many of the systems presented beyond have little resemblance to any igneous rock composition, but they are necessary to an understanding of the equilibria in the more complex systems that do approach igneous rock compositions. A phase diagram is an exceedingly concise method of reporting, in a graphical "short hand", a tremendous amount of data. Only a few of the more significant petrological aspects can be mentioned in the descriptions; for further discussions of the diagrams given, the reader is directed to the original references. A recent paper by SCHAIRER (1957) gives a more complete

coverage of most of the systems discussed beyond. All diagrams are in terms of weight per cent and degrees Centigrade, and unless stated otherwise, all are given essentially as published. On the ternary diagrams the direction of decreasing temperature is indicated by arrows on the boundary curves, and light lines (Alkemade lines) dividing the system up into composition triangles have been drawn.

Binary Oxide Systems

K_2O–SiO_2. The portion of the system K_2O–SiO_2 from SiO_2 to the compound $K_2O \cdot SiO_2$ was studied by KRACEK *et al.* (1929), and by KRACEK (1930a). These studies showed the existence of two intermediate compounds, $K_2O \cdot 2SiO_2$ and

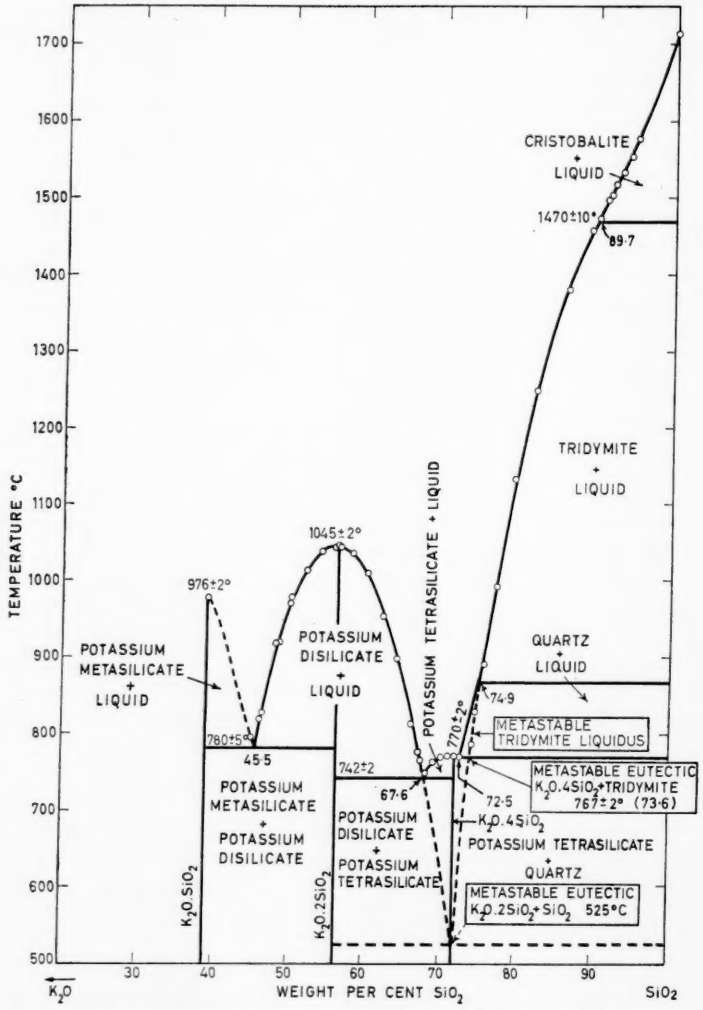

Fig. 4. Equilibrium diagram of the system $K_2O \cdot SiO$–K_2O. (After KRACEK *et al.*)

$K_2O \cdot 4SiO_2$. The revised diagram, as given by KRACEK *et al.*, (1937) is reproduced in Fig. 4, with the addition of the metastable eutectic between $K_2O \cdot 2SiO_2$ and SiO_2, as deduced by MOREY and FENNER (1917). It should be noted also how the addition of K_2O to SiO_2, to the extent of 27·5 per cent, brings the liquidus of SiO_2 down from the melting point (1713°C) to 770°C—averaging 34° drop for each per cent K_2O.

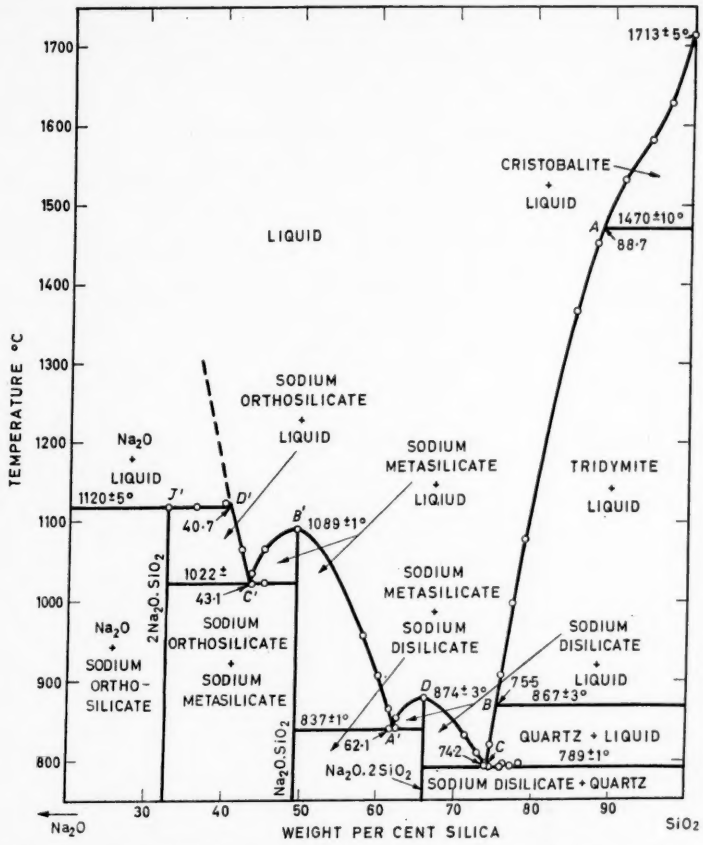

Fig. 5. Equilibrium diagram of the system Na_2O–SiO_2. (After KRACEK.)

Na_2O–SiO_2. The high-silica portion of this system (above the compound $Na_2O \cdot SiO_2$), was investigated by MOREY and BOWEN (1924), and additional data were added by BOWEN and SCHAIRER (1929b) and by BOWEN *et al.* (1930). The system was restudied and extended to include the compound $2Na_2O \cdot SiO_2$, by KRACEK (1930a, b and 1939). His phase diagram for the system is given as Fig. 5. The addition of Na_2O is seen to lower the liquidus of SiO_2 36° for each per cent Na_2O. The low-melting mixtures in the vicinity of the compound $Na_2O \cdot 2SiO_2$ are sluggish to crystallize and are rather viscous.

CaO–SiO_2. This rather complex system (Fig. 6) was reported by RANKIN and WRIGHT in their study of the system CaO–Al_2O_3–SiO_2 (1915), and various

portions of their diagram have been revised by numerous later investigators (see LEVIN *et al.*, 1956, p. 48 and SCHAIRER, 1957). There are four binary compounds in the system, and at least two of these have two or more modifications. The lowest liquidus temperature in the system is still rather high (1436°), in spite of the very abrupt drop from $2CaO \cdot SiO_2$ to the rankinite–pseudowollastonite

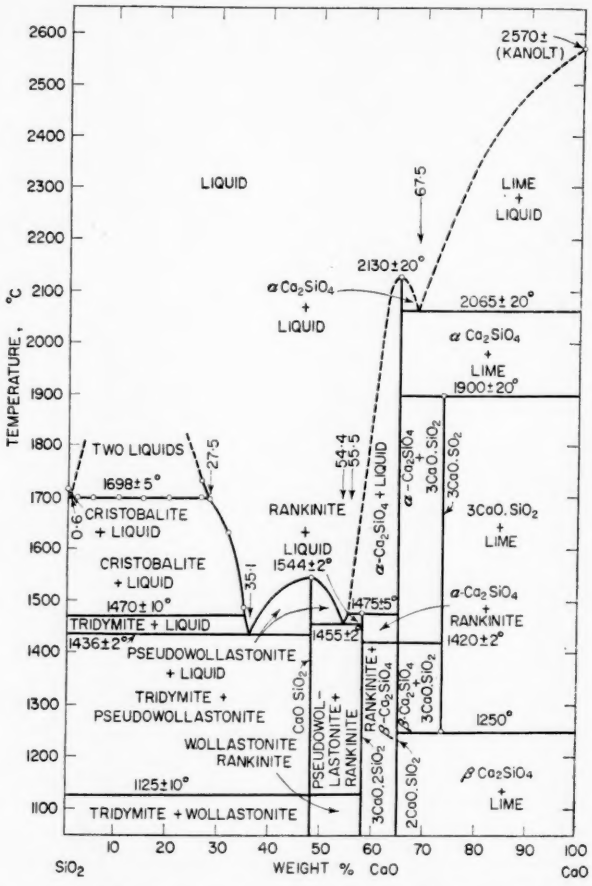

Fig. 6. Equilibrium diagram of the system $CaO–SiO_2$. (After RANKIN and WRIGHT, GREIG, and others.)

eutectic (see Fig. 6). The decrease in the liquidus of silica is not as abrupt as with the alkalis K_2O and Na_2O, in that a field of liquid immiscibility intersects the liquidus surface from 0·6 per cent CaO to 27·5 per cent CaO. This has the effect of negating the drop in the SiO_2 liquidus that would have taken place for CaO additions in this range, if no immiscibility had occurred.

$MgO–SiO_2$. The system $MgO–SiO_2$ is considerably simpler than the system $CaO–SiO_2$. It is shown in Fig. 7 as reported by BOWEN and ANDERSEN (1914)

and modified by GREIG (1927). There are only two compounds in the system, a pyroxene ($MgO \cdot SiO_2$) and an olivine ($2MgO \cdot SiO_2$), and the liquidus temperatures are high throughout, never falling below that of the eutectic between $MgO \cdot SiO_2$ and SiO_2 at 1543°. A region of liquid immiscibility, similar to that in the system CaO–SiO_2, extends (at the liquidus) from 0·8 per cent to 30·5 per cent MgO, causing the rate of drop, in the range from *B* to *D* (Fig. 7) to be 38° for each °/₀ MgO. This system also illustrates the incongruent melting of

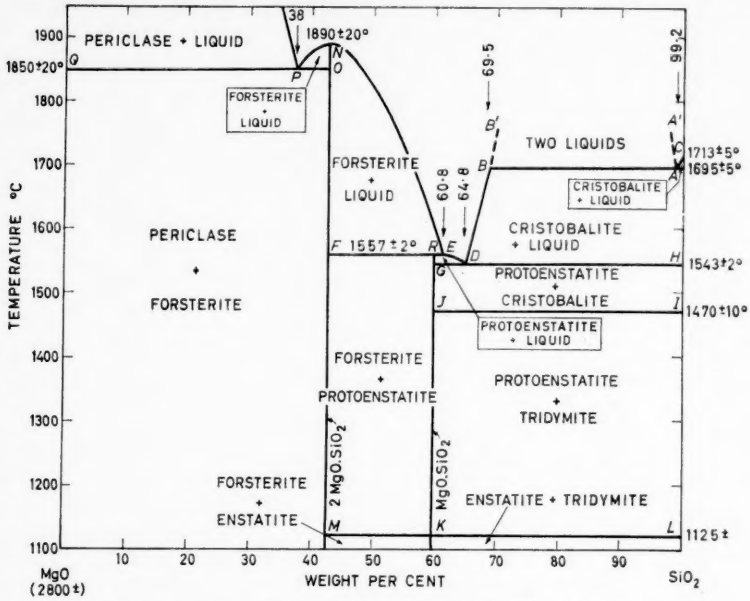

Fig. 7. Equilibrium diagram of the system MgO–SiO_2. (After BOWEN and ANDERSEN, and GREIG.)

the pyroxene $MgO \cdot SiO_2$ to form crystals of the olivine $2MgO \cdot SiO_2$ (forsterite) and a more siliceous liquid. As will be shown beyond, many silicate compounds melt incongruently, and with a few exceptions, always to form a more siliceous liquid.

This and other diagrams involving the compound $MgO \cdot SiO_2$ have been relabelled to indicate the relationships found by SCHAIRER (1954) for the various forms of this compound. He showed that enstatite, the low-temperature form, inverts at 1125, + 0 − 25°, to protoenstatite, which is stable to the liquidus; on quenching protoenstatite goes through a snap inversion to clinoenstatite.

FeO–SiO_2. The phase diagram for this system is even simpler than the foregoing, but the variable valence of iron resulted in experimental difficulties that were not solved until much later. BOWEN and SCHAIRER (1932) found that it was possible to melt ferrous iron-bearing batches in pure metallic iron crucibles in an inert (nitrogen) atmosphere. There was always a small amount of ferric iron present (usually stated in terms of weight per cent Fe_2O_3), representing an equilibrium between the ferrous, ferric and metallic iron species. Such systems

should therefore be considered to lie in a more general system with Fe and Fe_2O_3 as components. There is only one compound in the system, the iron olivine fayalite ($2FeO \cdot SiO_2$). The hypothetical iron ortho-pyroxene $FeO \cdot SiO_2$, named ferrosilite, does not occur in this system and has not been synthesized, although a clino-pyroxene of this composition has been found in nature (BOWEN, 1935a) and KURTSEVA (1953) has reported slag pyroxenes containing up to 76 per cent ferrosilite "molecule". The diagram for the system, with all iron calculated as FeO, is given in Fig. 8 from BOWEN and SCHAIRER (1932). The actual amounts of

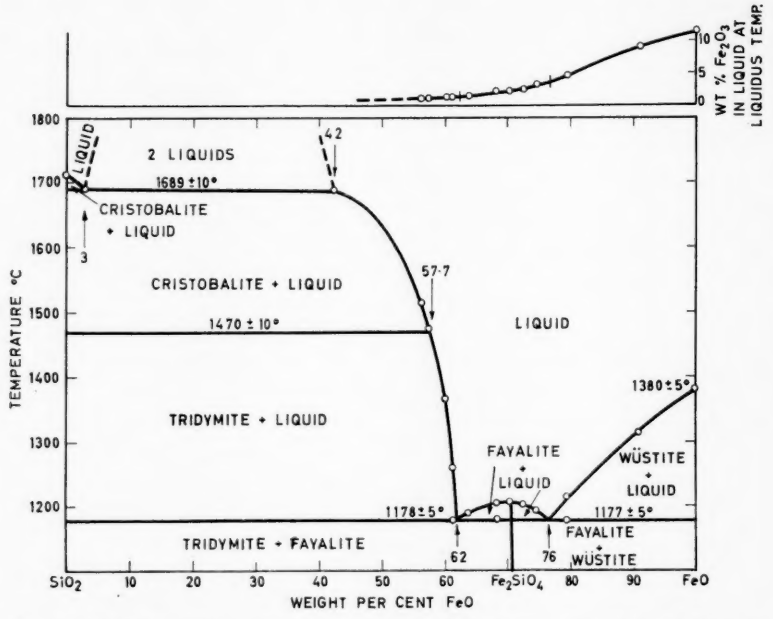

Fig. 8. Equilibrium diagram of the system FeO–SiO_2, constructed by calculating all iron oxides in the liquids to FeO. Upper figure gives actual amounts of Fe_2O_3 in liquids at liquidus temperatures, indicating extent of departure from binary character. (After BOWEN and SCHAIRER, and GREIG.)

Fe_2O_3 found are indicated on the upper figure, which shows the manner in which the amount of Fe_2O_3 is strongly influenced by the total amount of iron, as FeO, in the batch. This relationship holds true in all systems with FeO. The high-silica portion, showing liquid immiscibility, has been taken from the work of GREIG (1927b).

Although similar in many ways to the systems CaO–SiO_2 and MgO–SiO_2, several features of the system FeO–SiO_2 contrast strongly with the other two. Thus the addition of FeO is not very effective in lowering the liquidus of silica, until approximately 50 per cent has been added (a point of great importance in the use of refractories in the steel industry). The iron olivine, fayalite, melts at 685° lower than its magnesian equivalent, forsterite, and this results in very much lower liquidus temperatures here (the two eutectics occur at 1177° and

1178°) than in the systems with CaO and MgO. Viscosity, which is not indicated on the diagram as it is a rate property, is low throughout most of the system, resulting in rapid crystallization and very short (< 1 hr) equilibration times, even with the low-temperature melts.

Fe_2O_3–SiO_2. The available data indicate that this system would require large oxygen pressures to maintain the iron in the ferric state (MUAN, 1955). Apparently it would consist of a large region of immiscible liquids, and small fields of hematite and silica (GREIG, 1927a).

Al_2O_3–SiO_2. The phase diagram for this system (Fig. 9) is from BOWEN and GREIG (1924), with a modification of the eutectic temperature based on the work

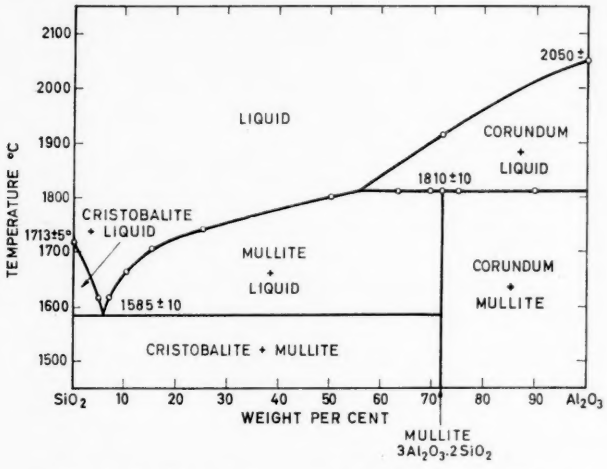

Fig. 9. Equilibrium diagram of the system Al_2O_3–SiO_2. (After BOWEN and GREIG.)

of SCHAIRER and BOWEN in the systems K_2O–Al_2O_3–SiO_2 (1955) and Na_2O–Al_2O_3–SiO_2 (1956). The eutectic, originally given as 1545°C, has been raised to 1595° ± 10°C. The original figure was too low probably because of small amounts of alkalies as impurities (SCHAIRER, 1957, p. 217). Even at these temperatures the viscosities are high. There is still some disagreement among various workers concerning the melting of the compound mullite ($3Al_2O_3 \cdot 2SiO_2$). BOWEN and GREIG (1924) found this to be an incongruently-melting compound (see Fig. 9), but BAUER *et al.* (1950), report synthesis of the compound by flame fusion, and TOROPOV and GALAKHOV (1951 and 1953) report that it melts congruently at 1890°C, and has a eutectic with Al_2O_3 at 1850° and 78 per cent Al_2O_3. They explain the evidence of incongruent melting, found by Bowen and Greig, on the basis of rapid volatilization of silica, leaving excess Al_2O_3 behind to form corundum. The data on the boundary line between the fields of corundum and mullite in the systems with K_2O and Na_2O (SCHAIRER and BOWEN, 1955 and 1956) appear to point toward an incongruent melting for mullite, however. The compound also takes excess Al_2O_3 in solid solution, but the limits of this are still in question (see SHEARS and ARCHIBALD, 1954; SCHAIRER and BOWEN, 1955, p. 690).

Ternary Oxide Systems

CaO–Al_2O_3–SiO_2. The equilibrium diagram for this system is given in Fig. 10. It is taken from the work of RANKIN and WRIGHT (1915), as modified by the work of BOWEN and GREIG (1924), GREIG (1927b), BOWEN *et al.* (1933b), and others. The diagram, in this form, first appeared in SCHAIRER (1942).

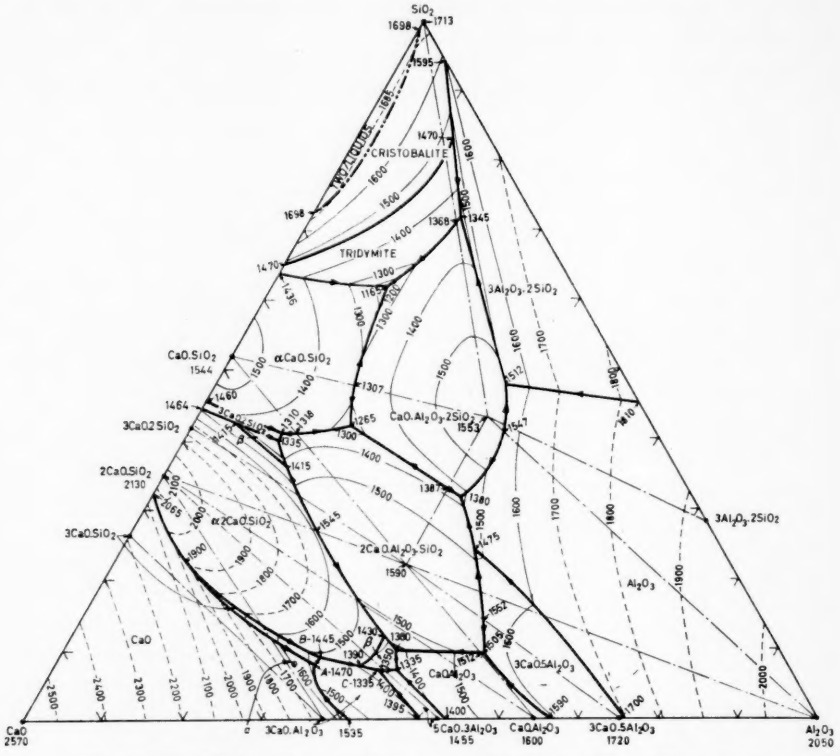

Fig. 10. Equilibrium diagram of the system CaO–Al_2O_3–SiO_2. Diagram of RANKIN and WRIGHT, revised (see text).

The system is complicated by two series of binary compounds, four in each of the systems CaO–SiO_2 and CaO–Al_2O_3, plus the compound mullite ($3Al_2O_3 \cdot 2SiO_2$), and two ternary compounds $2CaO \cdot Al_2O_3 \cdot SiO_2$ (gehlenite) and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (anorthite).

Although some of the composition triangles drawn on the diagram outline simple ternary subsystems with a ternary eutectic point located within each (e.g. $CaO \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$–$SiO_2$), six of the composition triangles shown have their corresponding ternary points outside of their respective triangles, i.e. they have ternary peritectic points (or ternary *reaction* points). This can result in rather unusual crystallization paths, and very erratic amounts of crystallization with a steadily decreasing temperature, as illustrated by Fig. 2 for the point "a" at 62·2 per cent CaO, 30·2 per cent Al_2O_3 and 7·6 per cent SiO_2. On cooling, the liquid in this composition passes through two ternary peritectic

points, *A* and *B*, very close to each other (see points *A* and *B* on Fig. 10), at which points the bulk of the crystallization takes place. At point *A*, at 1470°, all of the early-formed CaO crystals (5 per cent) react with liquid of composition *A* to form $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ (along with simultaneous additional, direct crystallization from the liquid). At point *B*, at 1455°, all the $3CaO \cdot SiO_2$ crystals react with liquid of composition *B* (and there is additional direct crystallization from the liquid) to form $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$. At this

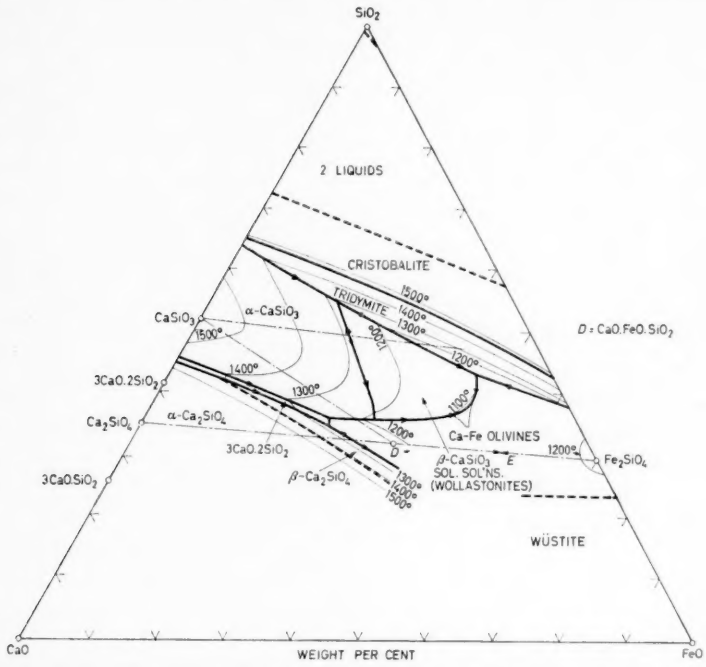

Fig. 11. Equilibrium diagram of part of the system $CaO–FeO–SiO_2$. There is a small amount of Fe_2O_3 in all liquids. (After BOWEN, SCHAIRER and POSNJAK.)

point there is only 12 per cent liquid left, the last 5 per cent of which crystallizes at the ternary eutectic point *C*. (As with all the diagrams of phase per cent vs. temperature presented here, the percentages are best obtained by scaling a much larger copy of the diagram.)

$CaO–FeO–SiO_2$. This system is shown in Fig. 11, taken from the work of BOWEN *et al.* (1933a and b). There are several important solid–solution series in this system, occurring along binary (or practically binary) subsystems through the ternary system. Diagrams for these are given in Figs. 12 and 13, for the system $2CaO \cdot SiO_2–2FeO \cdot SiO_2$ (the orthosilicate or "olivine" join), and the system $CaO \cdot SiO_2–FeO \cdot SiO_2$ (the metasilicate or "pyroxene" join). In each of these two systems, there is an intermediate compound with a 1:1 mole ratio of Ca:Fe. In the system $2CaO \cdot SiO_2–2FeO \cdot SiO_2$ the compound $CaO \cdot FeO \cdot SiO_2$ (point *D* in Fig. 12) melts congruently and forms a solid solution on both the Ca-rich and Fe-rich sides. Between $CaO \cdot FeO \cdot SiO_2$ and $2FeO \cdot SiO_2$ there is a

continuous series of solid solutions with a low-temperature minimum at point *E*, rich in iron. In the system $CaO \cdot SiO_2$–$FeO \cdot SiO_2$, the compound $CaO \cdot FeO \cdot 2SiO_2$ (hedenbergite) breaks down, upon heating, at 965° (point *H'* Fig. 13) to form a wollastonite ($\beta CaO \cdot SiO_2$) solid solution, of the same composition, which starts to melt incongruently at about 1120° to form tridymite and liquid (ternary equilibria). The progress of crystallization in this system is

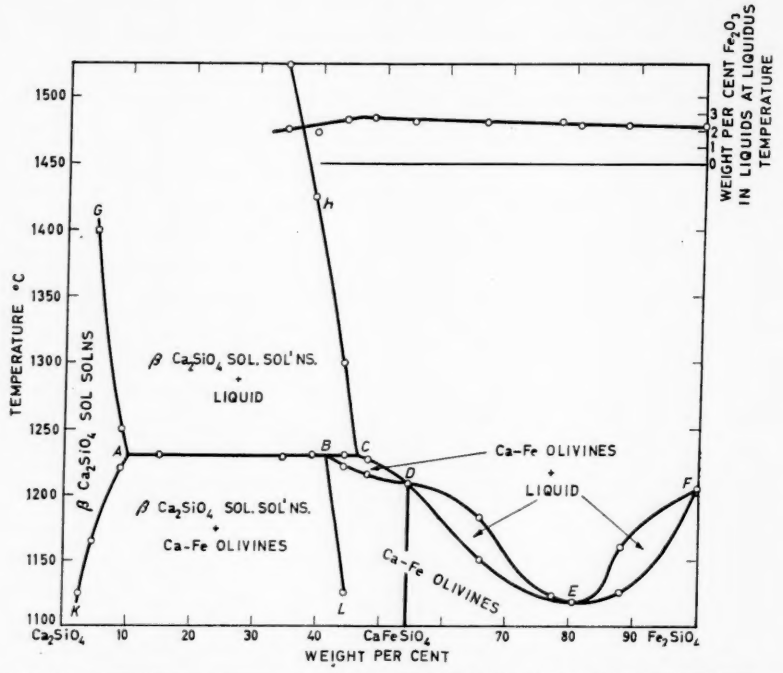

Fig. 12. Equilibrium diagram of the system $2CaO \cdot SiO_2$–$2FeO \cdot SiO_2$ (orthosilicate join in the system CaO–FeO–SiO_2). (After BOWEN, SCHAIRER and POSNJAK.)

complex, due to these two solid solution series, and has been outlined by a series of fifteen isothermal planes (BOWEN *et al.*, 1933b). The very marked drop in liquidus temperatures toward the iron silicate fayalite should be noted.

MgO–FeO–SiO_2. This system was studied by BOWEN and SCHAIRER (1935), and their phase diagram is presented in Fig. 14. As with all systems including FeO as a component, a small amount of Fe_2O_3 is present in all liquids, representing equilibrium between the melt and the metallic iron crucible (see Fig. 15). The system is rather closely related to that for the system CaO–FeO–SiO_2, in that the metasilicate and orthosilicate binary (or partially binary) subsystems also show solid solution series. As in the system CaO–FeO–SiO_2, the precise melting relations in this system are best seen with the aid of a series of isothermal sections, as given by BOWEN and SCHAIRER (1935). The orthosilicate system forsterite–fayalite, a simple binary solid solution series (see Fig. 16), was first presented and its application to the intrusion of dunite given by BOWEN and SCHAIRER (1933). The metasilicate (pyroxene) system is complicated by virtue

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of considerable areas of ternary (i.e. non-binary) equilibrium (see Fig. 17), and by the inversion between ortho- and clino-pyroxene. Although synthetic pyroxenes containing up to nearly 90 per cent of the $FeO \cdot SiO_2$ "molecule" have been made in the laboratory, and crystals with as much as 76 per cent have been found in slags (KURTSEVA, 1953), the pure ortho-pyroxene ferrosilite has not

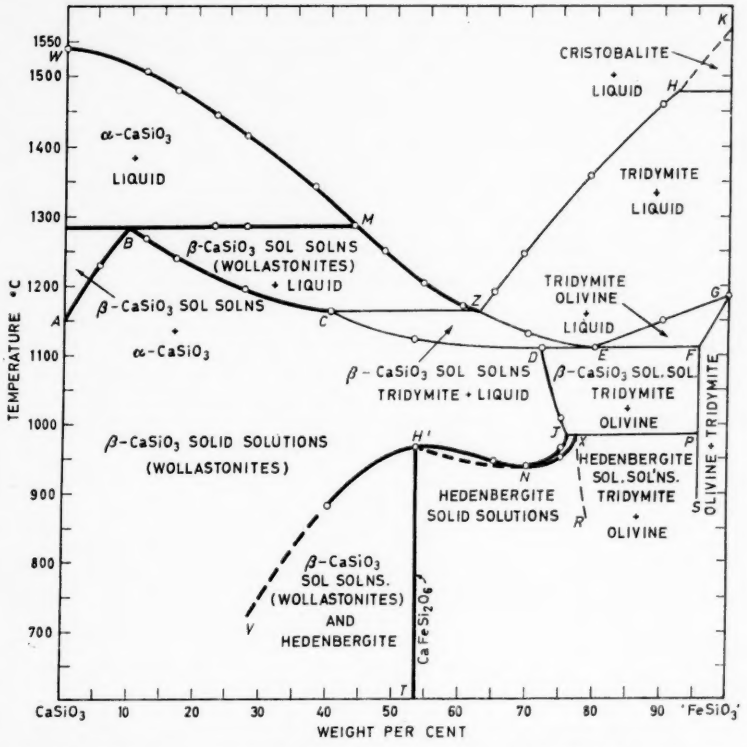

Fig. 13. Equilibrium diagram of mixtures in the system CaO–FeO–SiO_2 with a metasilicate ratio. Heavy curves refer to binary equilibrium and light curves to ternary equilibrium–binary and ternary, respectively, only when small amounts of Fe_2O_3 present in liquids are treated as FeO. (After BOWEN, SCHAIRER and POSNJAK.)

been found in nature. BOWEN (1935a) reported the occurrence of apparently pure clinoferrosilite in the lithophysae of obsidians.

CaO–MgO–SiO_2. The diagram for this system, with isotherms, is given as Fig. 18. The system shows four ternary compounds, the metasilicate pyroxene diopside ($CaO \cdot MgO \cdot 2SiO_2$), the orthosilicates monticellite ($CaO \cdot MgO \cdot SiO_2$), and merwinite ($3CaO \cdot MgO \cdot 2SiO_2$), and the compound akermanite ($2CaO \cdot MgO \cdot 2SiO_2$). This diagram is based on the general study of the system by FERGUSON and MERWIN (1919), and on the work of BOWEN (1914) on the subsystem diopside–forsterite–silica, GREIG (1927) on the high-silica region of immiscibility, SCHAIRER and BOWEN (1942), and OSBORN (1942), on the subsystem $CaO \cdot SiO_2$–diopside, and OSBORN (1943) on the stability of merwinite.

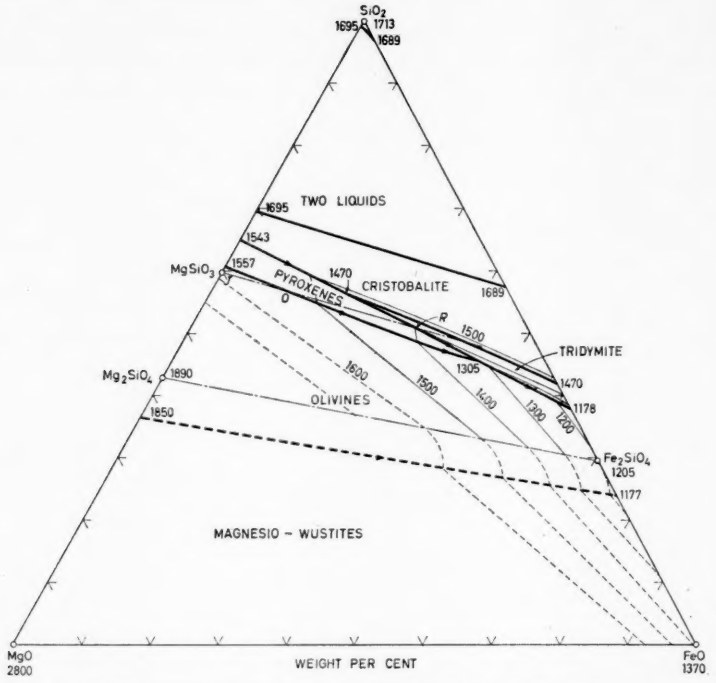

Fig. 14. Equilibrium diagram of the system, MgO–FeO–SiO_2. There is a small amount of Fe_2O_3 in all liquids in this system, as shown in Fig. 15. (From BOWEN and SCHAIRER.)

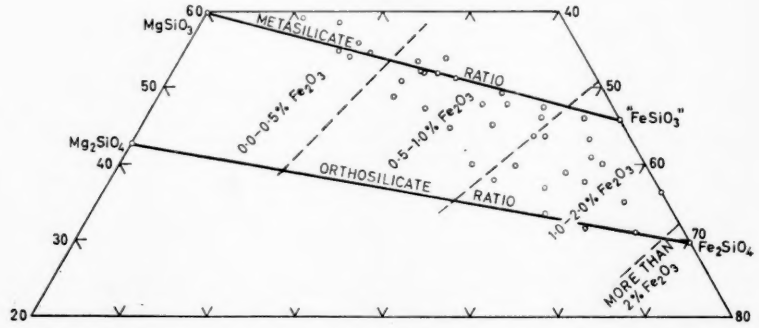

Fig. 15. Diagram showing the approximate Fe_2O_3 content of liquid mixtures of MgO, SiO_2 and Fe oxide, in equilibrium with metallic iron. The position of the figure in the general triangle is readily made out by comparison with Fig. 14. (After BOWEN and SCHAIRER.)

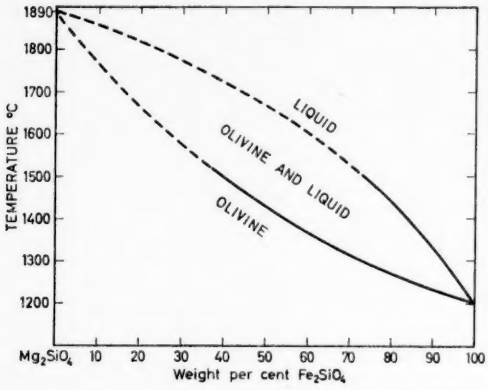

Fig. 16. Equilibrium diagram of the system $2MgO \cdot SiO_2$–$2FeO \cdot SiO_2$ (orthosilicate join in the system MgO–FeO–SiO_2). (After BOWEN and SCHAIRER.)

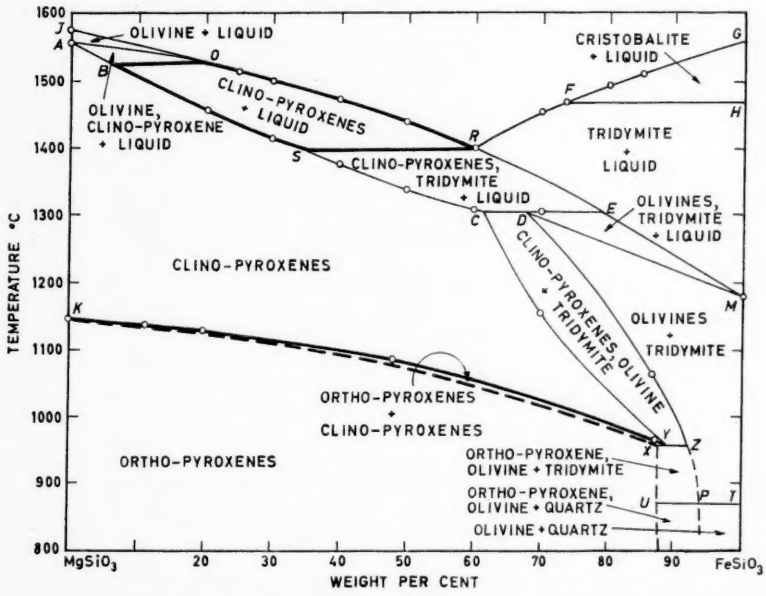

Fig. 17. Equilibrium diagram of mixtures of metasilicate ratio in the system MgO–FeO–SiO_2. Heavy curves refer to binary equilibrium and light curves to ternary equilibrium (binary and ternary respectively only when small amounts of Fe_2O_3 present in liquids are treated as FeO). "Clino-pyroxene" here refers to protoenstatite (SCHAIRER, 1954). (After BOWEN and SCHAIRER.)

Additional portions were restudied by RICKER and OSBORN (1954), and Fig. 18 is taken from their work. The lowest eutectic in the system is that between $\beta CaO \cdot SiO_2$ solid solutions, a diopsidic pyroxene and tridymite, at 1320°. The odd-shaped field for the pyroxenes is particularly interesting. Between $MgO \cdot SiO_2$ (clinoenstatite and protoenstatite) and $CaO \cdot MgO \cdot 2SiO_2$ (diopside) there is a series of solid solutions, almost continuous at high temperature, with a minimum

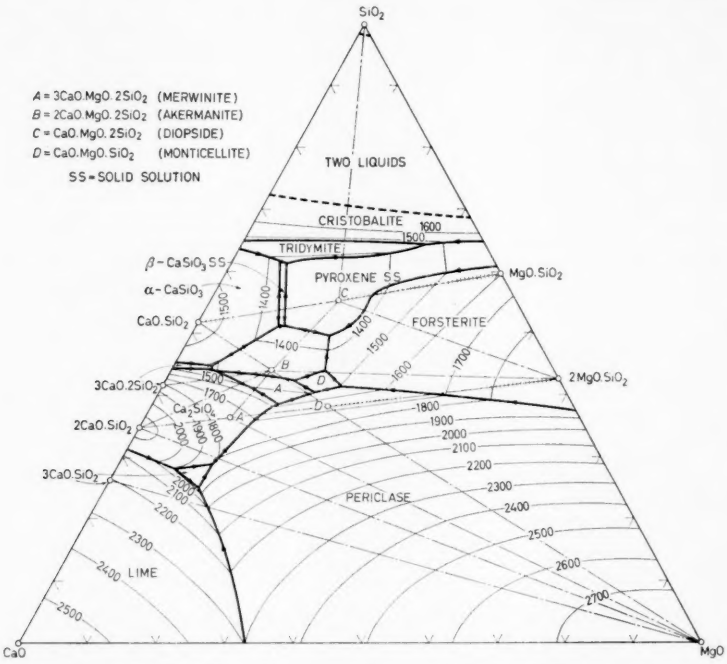

Fig. 18. Revised equilibrium diagram of the system CaO–MgO–SiO_2. Short cross lines along metasilicate and orthosilicate joins indicate maximum extent of solid solution. Mont. = monticellite; Merw. = merwinite. (After FERGUSON and MERWIN, GREIG, SCHAIRER and BOWEN, OSBORN, and RICKER and OSBORN.)

near diopside, and unmixing at lower temperatures (ATLAS, 1952; BOYD and SCHAIRER, 1957). In addition, one end of this system ($MgO \cdot SiO_2$) melts incongruently to form forsterite plus a more siliceous liquid, whereas the other end (diopside) melts congruently. The liquidus surface for diopside in the ternary system is exceedingly flat over the composition point of the compound, indicating extensive dissociation in the melt. This is one reason why the melting, of synthetic diopside provides a good temperature calibration point, as deviations from the stoicheiometric composition are not serious in their effect. There are ten binary and ternary compounds in this system, and a number show two or more modifications and extensive but partial solid solution. For a fuller discussion of these complexities and the extensive literature, see the original references and EITEL (1954a, pp. 656–667).

$MgO–Al_2O_3–SiO_2$. The system $MgO–Al_2O_3–SiO_2$ is complicated by the

presence of two ternary compounds cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), and sapphirine ($4MgO \cdot 5Al_2O_3 \cdot 2SiO_2$). In the original work by RANKIN and MERWIN (1918), only cordierite was found at the liquidus surface. FOSTER (1950) predicted that the compound sapphirine should occur at the liquidus surface in the system, and this was verified by KEITH and SCHAIRER (1952), whose diagram

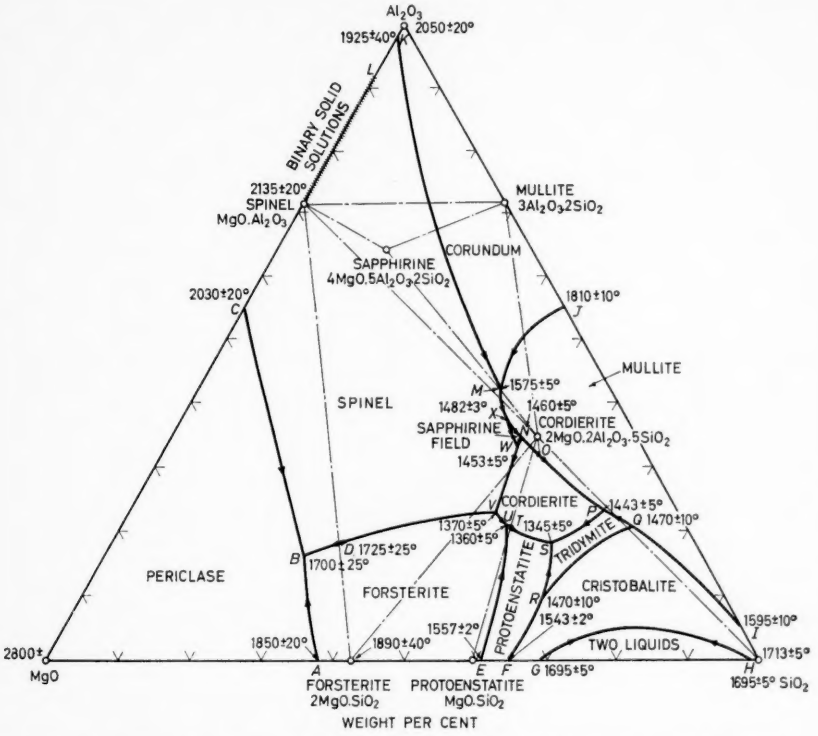

Fig. 19. Equilibrium diagram of the system MgO–Al_2O_3–SiO_2. (Diagram of RANKIN and MERWIN as modified by BOWEN and GREIG, GREIG, SCHAIRER, FOSTER, and KEITH and SCHAIRER.)

is presented (Fig. 19). This shows the liquidus relations between the ten phases found in the system, all of which occur in nature.

FeO–Al_2O_3–SiO_2. This system, as drawn by SCHAIRER and YAGI (1952), is presented as Fig. 20. There is a considerable similarity to the system MgO–Al_2O_3–SiO_2, in that there are iron analogs of the binary compounds forsterite and spinel, and of the ternary compound cordierite. The field of FeO is considerably smaller than that of MgO in the other system, as might be expected from the large difference (1420°) in the melting points. As with all silicate systems, the substitution of FeO for MgO lowers the liquidus throughout. Thus the lowest liquidus temperature in the system MgO–Al_2O_3–SiO_2, at the eutectic between silica, Mg–cordierite, and $MgO \cdot SiO_2$ is 1345° (point *S*, Fig. 19), whereas the lowest liquidus in the iron system is at the eutectic between silica,

Fe–cordierite, and $2FeO.SiO_2$ at 1083° (point *N*, Fig. 20). The large effect of oxygen pressure in the gas with which this system is equilibrated is shown by MUAN (1957).

$FeO–Fe_2O_3–SiO_2$. This system will be discussed here, not for its particular pertinence to igneous rock compositions, but for the important principles which it demonstrates. The system at 1600°C was sketched by GURRY and DARKEN (1950), and the entire liquidus surface below 1600° was determined by MUAN

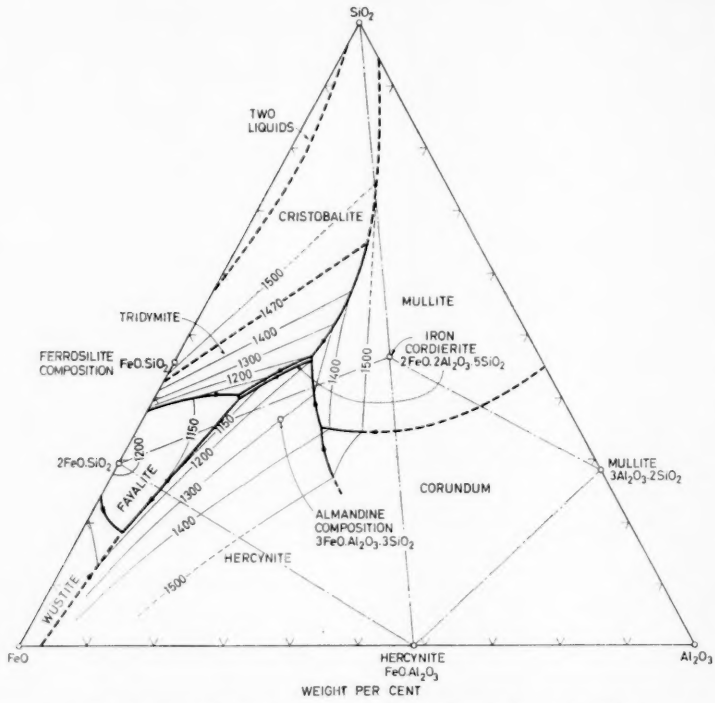

Fig. 20. Equilibrium diagram of the system $FeO–Al_2O_3–SiO_2$. (After SCHAIRER and YAGI.)

(1955). Fig. 21 (from Muan) shows the liquidus relations. In particular, it shows the incongruent melting of FeO, and $2FeO \cdot SiO_2$, to form metallic iron and a liquid enriched in oxygen, as indicated by the field of iron over the composition points for FeO and $2FeO \cdot SiO_2$. This field probably should extend up to the SiO_2 corner, indicating that all mixtures of FeO and SiO_2 will form some "Fe_2O_3", plus metallic iron, at equilibrium. This figure also shows the wide band of immiscibility in the silica-rich corner of the system and the low minimum temperature on the liquidus, 1140°, for the eutectic magnetite–fayalite–tridymite. Figure 22, also from Muan, is a plot of the oxygen pressures in the gas over the melts whose phase equilibria are recorded in Fig. 21. It is important to note the vast range in oxygen pressures involved in this system—over twelve orders of magnitude. KENNEDY (1948) made use of such relationships in an attempt to estimate the amount of hydrogen in the gas with respect

to which some Halemaumau basalts had presumably been equilibrated, using the ferrous/ferric ratio and the known dissociation of water. It is apparent from Fig. 22, however, that the isobars are not solely dependent on the FeO/Fe_2O_3 ratio, in this particular system.

K_2O–CaO–SiO_2 *and* Na_2O–CaO–SiO_2. The high liquidus temperatures characteristic of the binary system CaO–SiO_2 are brought down rapidly by the addition of K_2O, as shown in Fig. 23 from MOREY *et al.* (1930, 1931). Practically

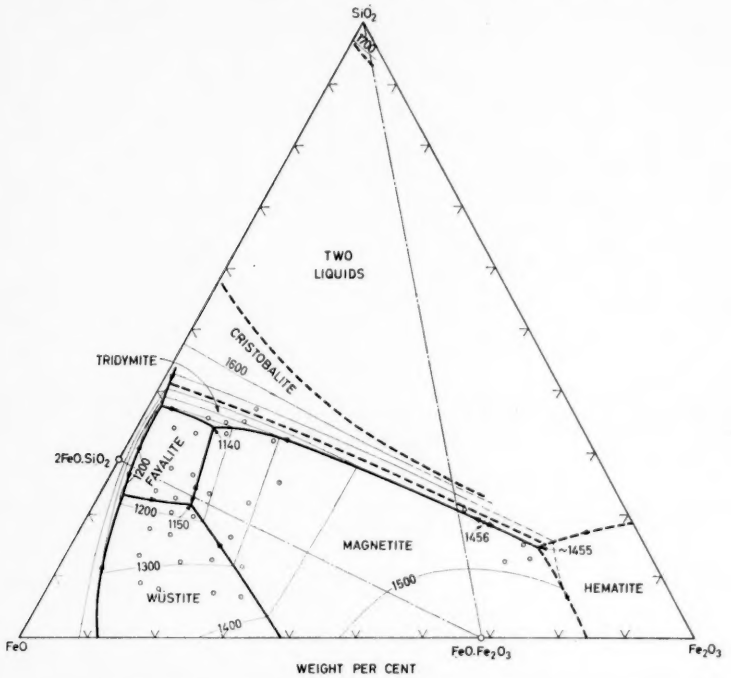

Fig. 21. Equilibrium diagram of the system FeO–Fe_2O_3–SiO_2. Circles represent compositions as shown by analysis, of mixtures at liquidus temperature. The tridymite–cristobalite boundary curve is dashed. (After MUAN.)

the entire high-silica portion of the ternary system has liquidus temperatures well under the lowest liquidus in the binary system CaO–SiO_2 (1355°). There are six ternary compounds in this part of the system K_2O–CaO–SiO_2, none of which are known in nature. Information on such phases is necessary, however, to understand phase equilibria in the more complex quaternary and quinary systems involving these three oxides. The viscosities are very high in the portions of this system having low liquidus temperatures, and crystallization is extremely sluggish. The lowest eutectic occurs at 720°C.

The system Na_2O–CaO–SiO_2 (Fig. 24) is similar, in its grosser aspects, to the system K_2O–CaO–SiO_2, but has only three ternary compounds in the portion studied (MOREY and BOWEN, 1925; MOREY, 1930), of which two, having ratios of 2:1:3 and 1:3:6, are also found in the system with potassia. Also as with the other system, the lowest liquidus temperatures (725°), between $Na_2O \cdot 2SiO_2$,

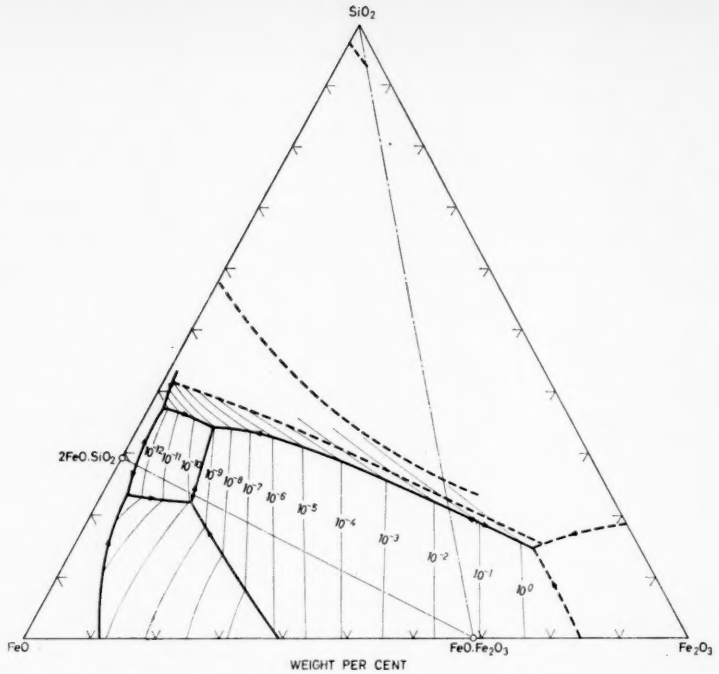

Fig. 22. Equilibrium diagram of the system FeO–Fe_2O_3–SiO_2. Heavy lines are boundary curves and light lines are lines of equal O_2 pressure for points on liquidus surface. (After MUAN.)

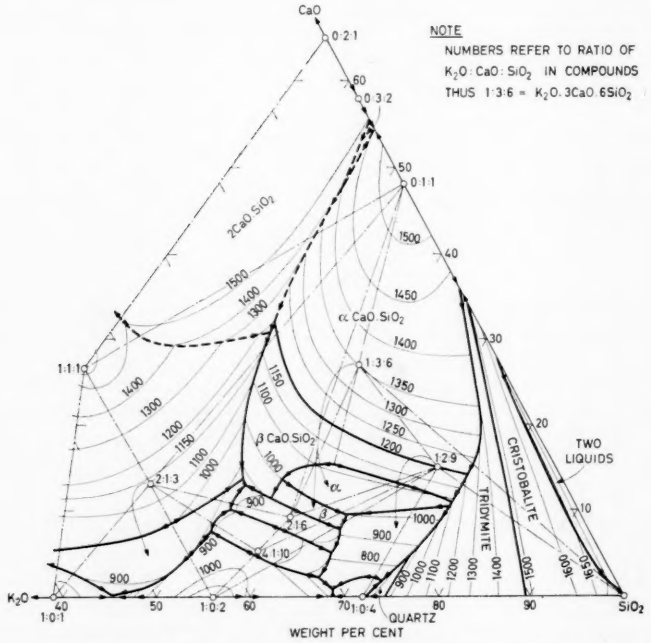

Fig. 23. Equilibrium diagram of part of the system K_2O–CaO–SiO_2. (Revised, after MOREY, KRACEK and BOWEN.)

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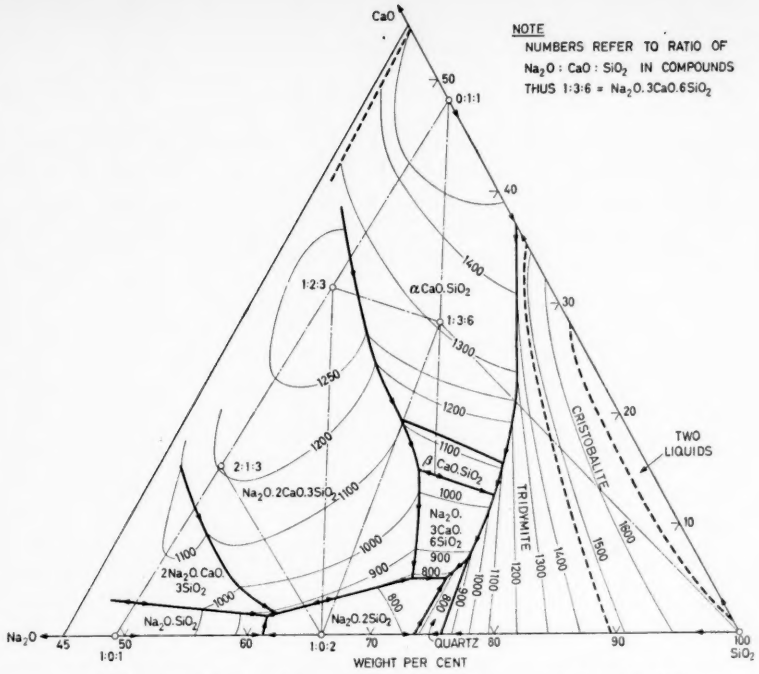

Fig. 24. Equilibrium diagram of part of the system Na_2O–CaO–SiO_2. (After MOREY and BOWEN.)

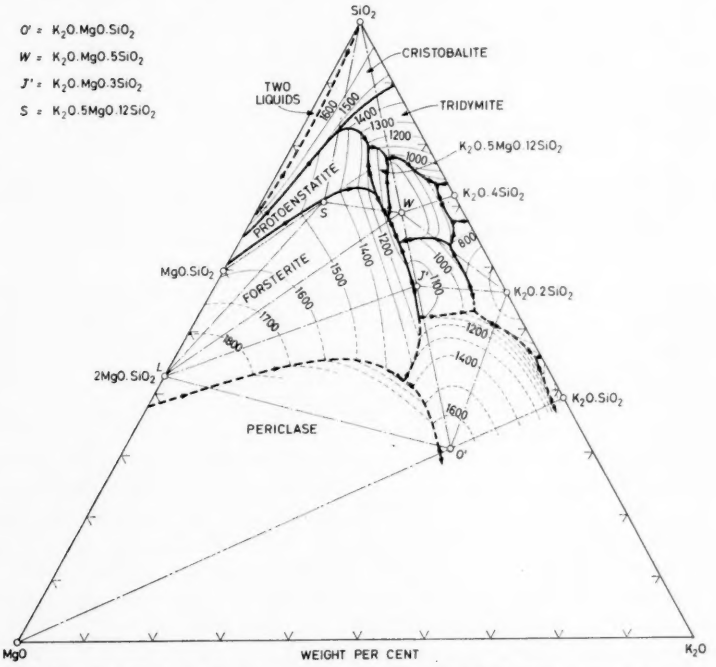

Fig. 25. Equilibrium diagram of the system K_2O–MgO–SiO_2. The tridymite field below 867° is metastable. (After ROEDDER.)

$Na_2O \cdot 3CaO \cdot 6SiO_2$ and quartz, occur in an area having exceedingly high viscosity.

K_2O–MgO–SiO_2 *and* Na_2O–MgO–SiO_2. The system K_2O–MgO–SiO_2 is shown in Fig. 25, after ROEDDER (1951a). It also shows a very rapid lowering of the liquidus temperatures of the binary system MgO–SiO_2, upon addition of K_2O (Fig. 3). Only one of the four ternary compounds in the system has the same ratios of alkali to alkaline earth to silica as were found in the systems with

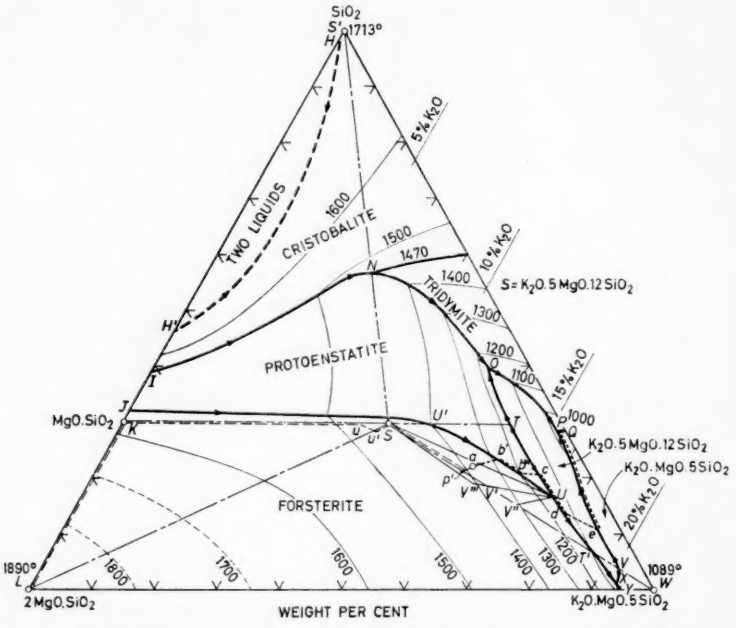

Fig. 26. Equilibrium diagram of the system $2MgO \cdot SiO_2$–$K_2O \cdot MgO \cdot 5SiO_2$–$SiO_2$. This is a portion of the general system K_2O–MgO–SiO_2, the oblique triangle LWS′ in Fig. 25. See text for description of crystallization path. (After ROEDDER.)

lime above. A compound of rather unusual formula, $K_2O \cdot 5MgO \cdot 12SiO_2$, appears in this system, and may be expected to occur in nature; its recognition may be difficult, however, as its optical properties are very similar to those of the quartz with which it might well occur. This compound occurs in the ternary subsystem $2MgO \cdot SiO_2$–$K_2O \cdot MgO \cdot 5SiO_2$–$SiO_2$, seen enlarged in Fig. 26. The crystallization of composition "a" in this subsystem has been discussed earlier (see Fig. 1 and Table 1). The two ternary compounds $K_2O \cdot MgO \cdot 5SiO_2$, and $K_2O \cdot MgO \cdot 3SiO_2$, found in this system, are also petrologically interesting. They are, in effect leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$) and kalsilite–kaliophilite ($K_2O \cdot Al_2O_3 \cdot 2SiO_2$), respectively, each with the two atoms of aluminium replaced by one magnesium and one silicon. In each case X-ray diffraction shows that they are apparently isostructural with their alumina analogues, and the striking similarity of the phase transitions observed, as well as the optical and crystallographic data, support this view. This would require, however, that

the Mg^{++} ion be in four-fold co-ordination in the two magnesium compounds, as it is substituting for a four-co-ordinated aluminium. Although the aluminium "end members" apparently crystallize at times in high-magnesium natural environments, magnesium does not seem to enter the natural minerals. The lowest temperature eutectic is near the compound $K_2O \cdot 4SiO_2$, at 685°.

The system Na_2O–MgO–SiO_2 was studied by BOTVINKIN and POPOVA (1937), and MANUILOVA (1937), and later was re-examined by SCHAIRER *et al.* (1953,

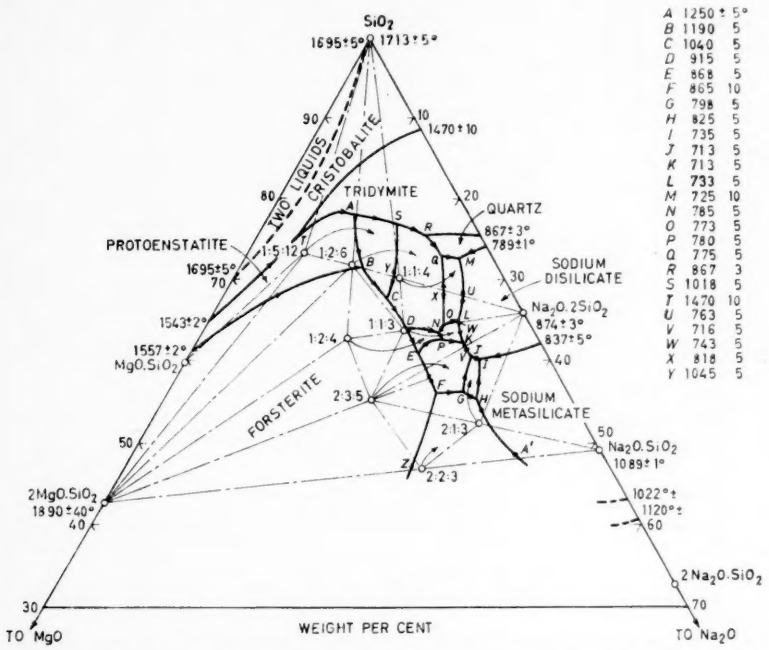

Fig. 27. Preliminary equilibrium diagram of the system Na_2O–MgO–SiO_2. (After SCHAIRER, YODER and KEENE.)

1954), with considerably different results. The preliminary diagram presented by SCHAIRER *et al.* (1954), is shown as Fig. 27. An additional compound, $Na_2O \cdot MgO \cdot SiO_2$, is reported by SCHAIRER (1957), but is not shown on Fig. 27. It is seen that although only the high-silica portion (> approximately 50 per cent SiO_2) has been studied, nine ternary compounds have been found. Three of these (1:1:1, 1:1:3 and 1:5:12) have counterparts in the system K_2O–MgO–SiO_2, but the other six do not. The large field of forsterite, the large distortion of the protoenstatite field toward the SiO_2 apex, and the low temperatures toward the alkali–silica side are all quite similar to the results found for the system K_2O–MgO–SiO_2. The lowest eutectics in the system Na_2O–MgO–SiO_2 occur near the compound $Na_2O \cdot 2SiO_2$, at 713°.

K_2O–FeO–SiO_2 *and* Na_2O–FeO–SiO_2. These two systems show striking similarities to the equivalent systems with MgO described above, and in fact, the study of the magnesia-bearing systems aided considerably in understanding

the experimentally more difficult iron systems. A preliminary diagram for the system $K_2O \cdot 2SiO_2$–FeO–SiO_2, the high-silica portion of the system K_2O–FeO–SiO_2, as given by ROEDDER (1952), is shown in Fig. 28, and a preliminary diagram for the system Na_2O–FeO–SiO_2 as given by SCHAIRER *et al.* (1953, 1954), is shown in Fig. 29. A previous study of the soda system by CARTER and IBRAHIM (1952) shows only one ternary compound, $Na_2O \cdot FeO \cdot SiO_2$, but Schairer's preliminary diagram indicates that the system is perhaps as

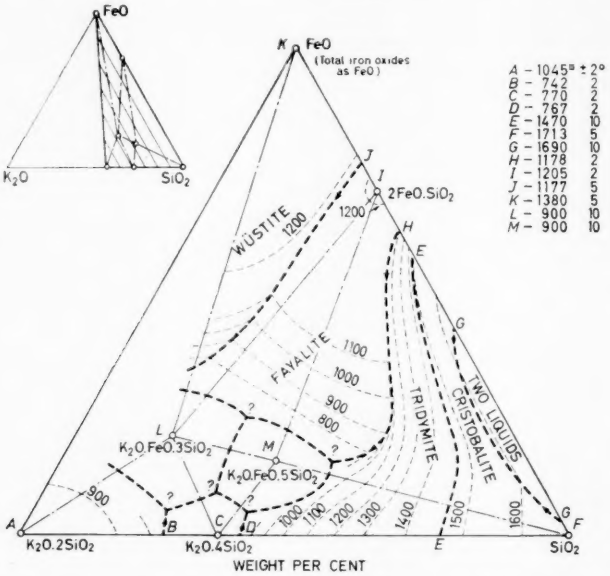

Fig. 28. Preliminary equilibrium diagram of the system $K_2O \cdot 2SiO_2$–FeO–SiO_2, subject to revision, showing liquidus relationships in equilibrium with metallic iron. Fe_2O_3 is present in all liquids. The insert shows the position of this system (shaded area) in the more general system K_2O–FeO–SiO_2. (After ROEDDER.)

complex as the analogous system Na_2O–MgO–SiO_2. Only two ternary compounds were found in the preliminary study of the system K_2O–FeO–SiO_2, having the ratios 1:1:3 and 1:1:5, just as in the system K_2O–MgO–SiO_2. These are the ferrous iron counterparts of the potassium aluminium silicates, kalsilite–kaliophilite and leucite, exactly as with the magnesium compounds above. As the iron compounds are apparently isostructural with the aluminium ones which have tetrahedrally co-ordinated aluminium ions, the Fe^{++} ion must occur in tetrahedral co-ordination in the iron compounds. Although none of the numerous ternary compounds found in the system with Na_2O have been specifically identified as to composition, several of these occur in the equivalent area of the system as the above potassium iron silicates. In both cases the lowest eutectics occur relatively near to the alkali–silica sideline, at temperatures $< 800°$, and at low-iron compositions. CARTER and IBRAHIM (1952) report the eutectic between $Na_2O \cdot 2SiO_2$, $2FeO \cdot SiO_2$ and SiO_2 to be at $< 500°C$. Also in both systems the field of fayalite extends to very high silica compositions.

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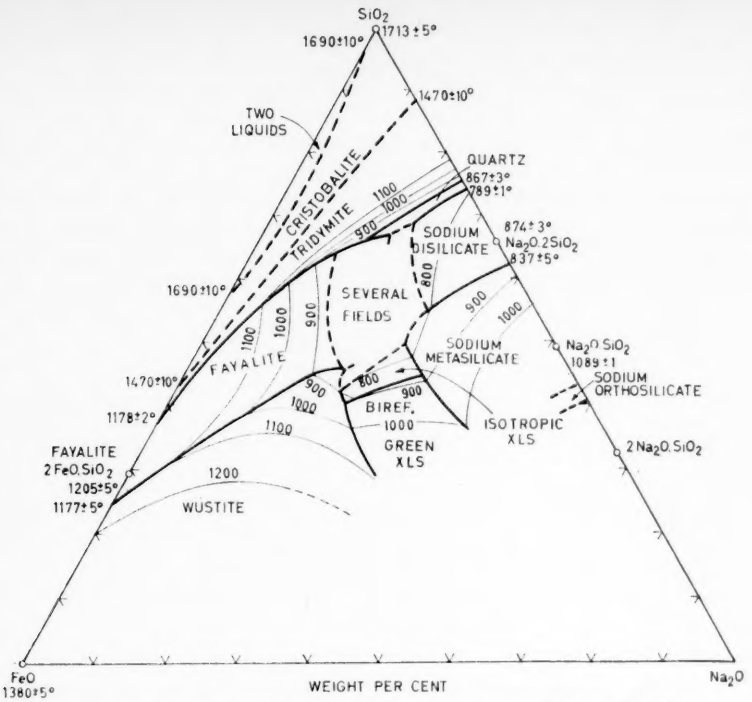

Fig. 29. Preliminary equilibrium diagram of the system Na_2O–FeO–SiO_2. (After SCHAIRER, YODER and KEENE.)

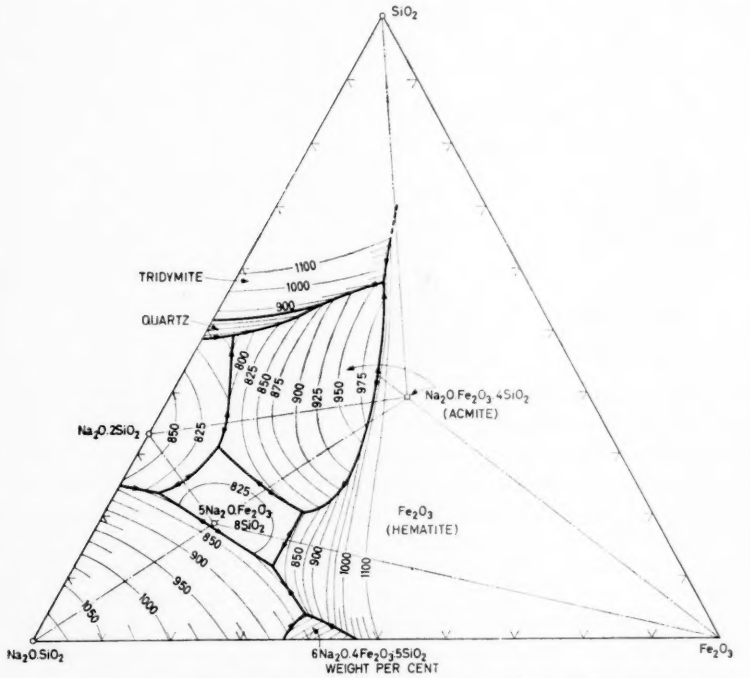

Fig. 30. Equilibrium diagram of the portion of the system Na_2O–Fe_2O_3–SiO_2 between $Na_2O \cdot SiO_2$, Fe_2O_3 and SiO_2. Equilibria along the sideline Fe_2O_3–SiO_2 are not known. (After BOWEN *et al.*)

Na_2O–Fe_2O_3–SiO_2. This system is of interest in that one of the ternary compounds found in it, $Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$, occurs also in nature as the pyroxene mineral acmite. The high-soda portion of the system $Na_2O \cdot SiO_2$–Fe_2O_3–SiO_2 has been studied by BOWEN and SCHAIRER (1929) and by BOWEN *et al.* (1930). The latter workers found two other ternary compounds, $5Na_2O \cdot Fe_2O_3 \cdot 8SiO_2$, and $6Na_2O \cdot 4Fe_2O_3 \cdot 5SiO_2$, as well as some evidence for the existence of the compound $2Na_2O \cdot Fe_2O_3 \cdot SiO_2$. Their diagram is reproduced as Fig. 30, in

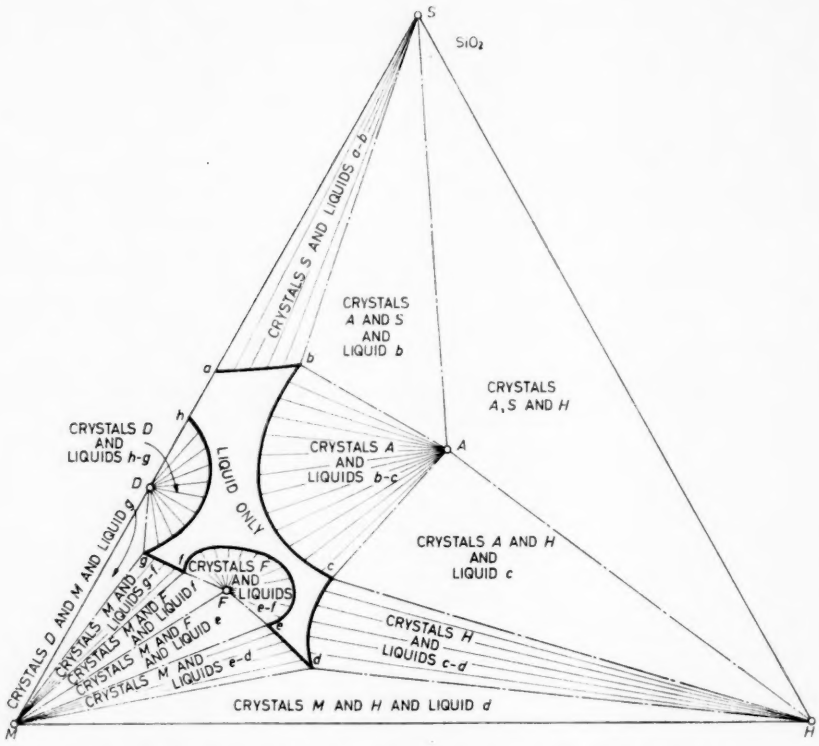

Fig. 31. Isothermal section at 825°C in the system Na_2O–Fe_2O_3–SiO_2. (After BOWEN *et al.*)

which small amounts of iron as Fe^{++} have been considered as Fe^{+++}. An isothermal section through this system at 825°, from the same authors, is given as Fig. 31. The low temperature trough near to the Na_2O–SiO_2 sideline is notable; although the differentiation of most igneous rocks results in a concentration of Fe relative to Mg, the lowest melting liquids in this system, as in the equivalent systems with K_2O and with FeO, are still rich in silica and alkali, and relatively poor in iron. Thus one can assume that of the two arms of Bowen's reaction series (BOWEN, 1922), the one that results in a net enrichment in alkalis in the residual liquids dominates over the one that results in a net enrichment in iron (BOWEN *et al.*, 1930, p. 450–454). Another significant consequence of the work on the system Na_2O–Fe_2O_3–SiO_2 is the discovery of the incongruent

melting of acmite, at 990°, to form hematite plus liquid. This requires that the acmite in rocks must have crystallized at this or lower temperatures, barring significant pressure effects and impurities.

K_2O–Al_2O_3–SiO_2 *and* Na_2O–Al_2O_3–SiO_2. These two diagrams are of considerable significance in petrology, as they include a number of important rock-forming minerals, the most important of which are the feldspars. The diagrams for both of these, with a brief discussion, were published by SCHAIRER and BOWEN

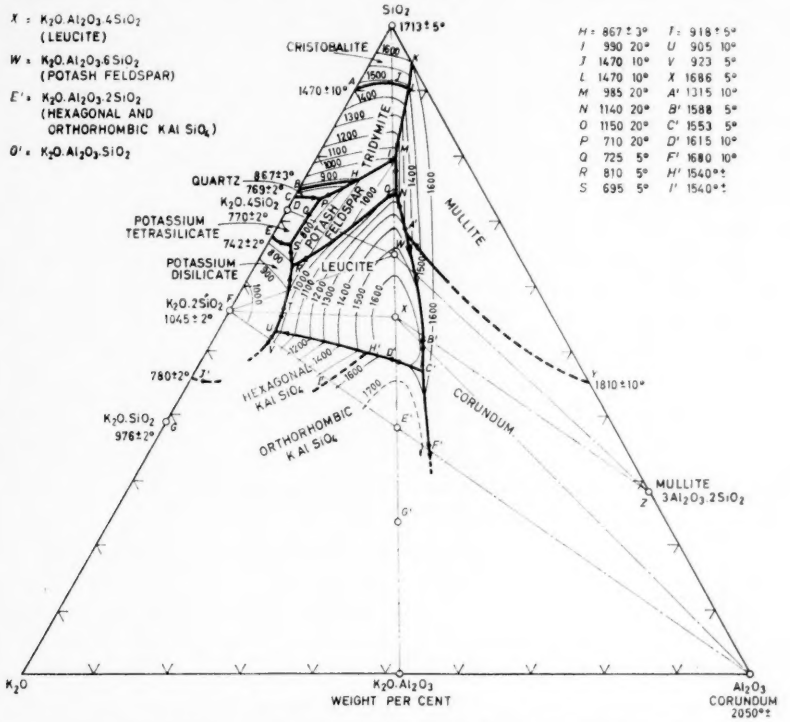

Fig. 32. Equilibrium diagram of the system K_2O–Al_2O_3–SiO_2. (After SCHAIRER and BOWEN.)

(1947b), and a full discussion of them will be found in SCHAIRER and BOWEN (1955 and 1956), from which Figs. 32 and 33 were taken. Only a few of the many features of these diagrams that should be pointed out can be considered here. The lowest temperature eutectics occur at 710° and 732°, respectively. In particular, the line of ternary compounds in each, including feldspathoids and feldspars, should be noted. The binary system between leucite and silica (line X–SiO_2 on Fig. 32) is shown in detail in Fig. 34, also from SCHAIRER and BOWEN (1955). From this it is seen that the incongruently melting compound potassium feldspar, and tridymite, form a eutectic at 990° ± 20° (point *I*, Fig. 32). The liquidus lines going down to this eutectic are dashed in Fig. 34, however, having been extrapolated from data in the ternary system, as the viscosities of the melts in this range of composition made precise determinations

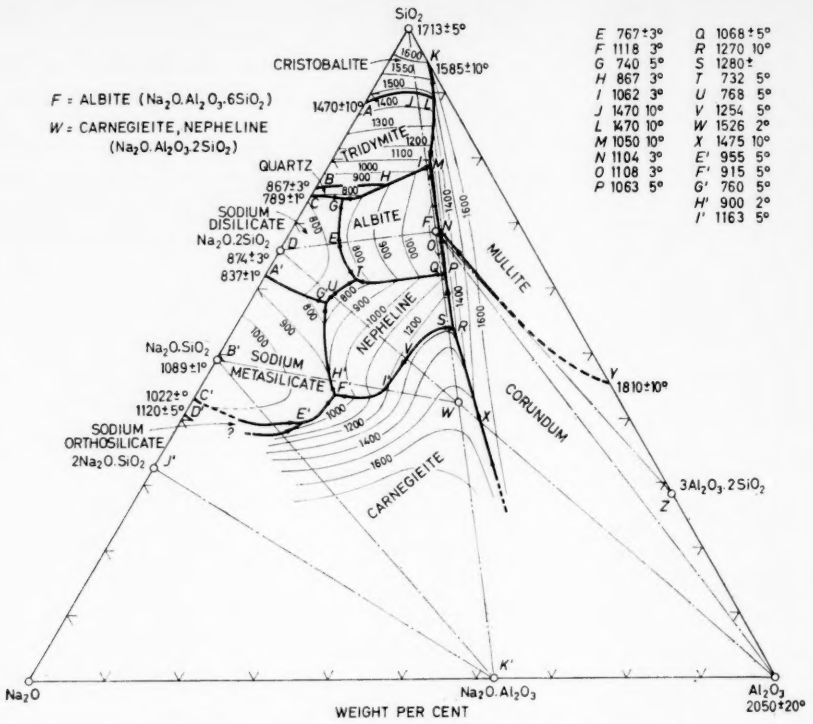

Fig. 33. Equilibrium diagram of the system Na_2O–Al_2O_3–SiO_2.
(After SCHAIRER and BOWEN.)

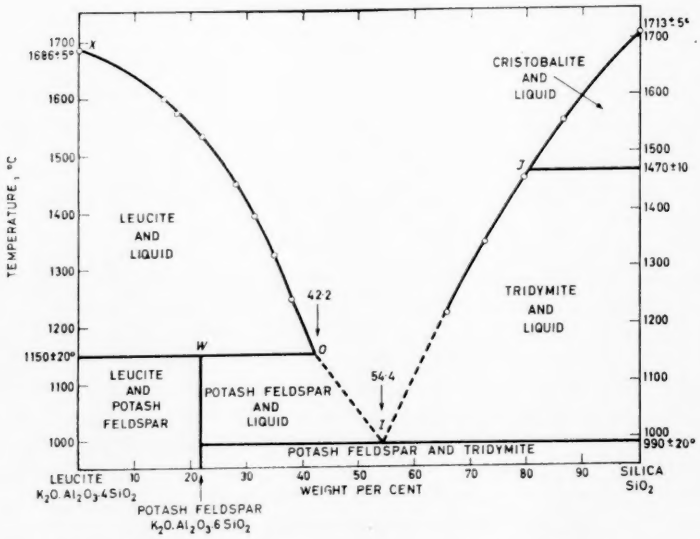

Fig. 34. Equilibrium diagram of the binary system leucite–silica.
(After SCHAIRER and BOWEN.)

practically impossible. Glasses of these compositions would not crystallize "dry" (i.e. without addition of water) even during periods as long as five years (SCHAIRER and BOWEN, 1955, p. 715). Yet a short distance from this line, in the ternary system, viscosities were considerably lower. These data, along with the sharp bend in the isotherms at the 1:1 K_2O:Al_2O_3 line, and the similar sharp bend in the lines of equal index of refraction (isofracts) for the glasses in this system (SCHAIRER and BOWEN, 1955, p. 714), indicate a strong dependence of the liquid properties on the molecular ratio of K_2O:Al_2O_3. Identical behaviour,

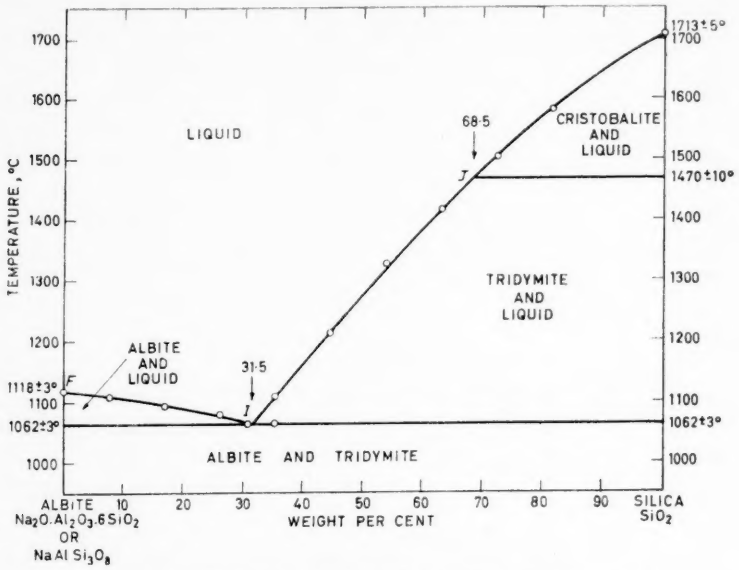

Fig. 35. Equilibrium diagram of the binary system albite–silica. (After SCHAIRER and BOWEN.)

but with lower viscosities, was noted in the system Na_2O–Al_2O_3–SiO_2 (SCHAIRER and BOWEN, 1956, p. 158), and a similar but much less obvious break was found in the isofracts and lines of equal glass density in the system K_2O–MgO–SiO_2, at the 1:1 molecular ratio of K_2O:MgO (ROEDDER, 1951a, p. 95). These phenomena are presumably related to the structure of the liquids, which must show maximum polymerization at the 1:1 molecular ratio.

The system Na_2O–Al_2O_3–SiO_2, from SCHAIRER and BOWEN (1956), is shown in Fig. 33. It has many things in common with the system K_2O–Al_2O_3–SiO_2. The most significant difference is in the lack of a sodium compound chemically equivalent to leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$). Although such a compound exists in nature (jadeite) and has been synthesized, it is not stable under the conditions of high temperature and one atmosphere pressure used in the determination of the system. The system albite–silica, line F–SiO_2 on Fig. 33, is shown in Fig. 35, also from SCHAIRER and BOWEN (1956). It is seen from this that the compound albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) melts congruently, and the eutectic with silica occurs at a lower ratio of silica/feldspar than occurs between potassium

feldspar and silica. Note also that the entire binary diagram was determined—no part of the liquidus has to be obtained by extrapolation, as was the case in the system with potassium. This is in consequence of the lower viscosities in the system with sodium, although a sharp rise in the viscosities of the liquids in the vicinity of the line albite–silica did occur.

One very unusual feature of this system is the subsystem albite–corundum. This is given in Fig. 36, from SCHAIRER and BOWEN (1956). It shows the

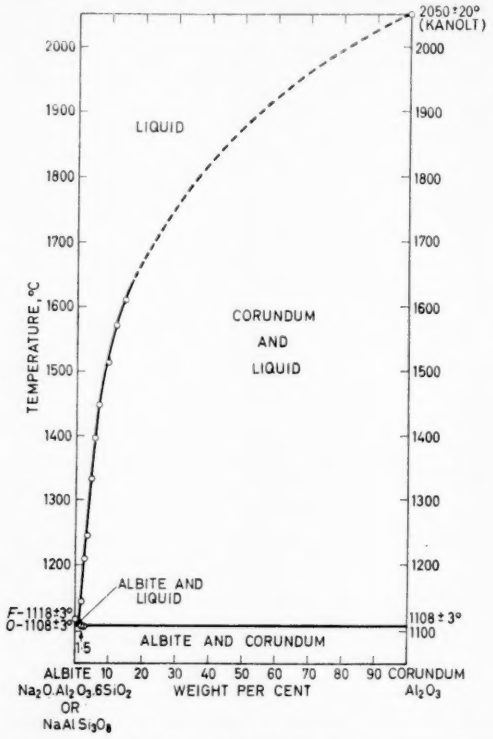

Fig. 36. Equilibrium diagram of the binary system albite–corundum. (After SCHAIRER and BOWEN.)

exceedingly small solubility of "excess" Al_2O_3 in albite melts; this is also apparent from the steep slope of the corundum, and mullite, fields in Fig. 33, where they approach the line representing a 1:1 molecular ratio of $Na_2O:Al_2O_3$.

Another unusual feature of the system Na_2O–Al_2O_3–SiO_2 is the interrelationships of the two forms of the compound $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$. The two forms, nepheline (low-temperature), and carnegieite (high-temperature), have an inversion at $1254° \pm 5°$ when pure but have widely differing tolerances for solid solution of various other substances. The curving inversion line *SVI'F'* (Fig. 33) shows the behaviour of this inversion depending upon the nature of the substance entering into solid solution. Thus point *S*, at 1280°, indicates that solid solution of albite *raises* the inversion temperature, and *I'* at 1163°, indicates that solid solution of $Na_2O \cdot SiO_2$ *lowers* the inversion temperature. Point

V, at 1254°, indicates that there is no effect on the inversion temperature from the insignificant amounts of solid solution of $Na_2O \cdot 2SiO_2$ in $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$. These differences, depending upon what material is entering into solid solution, and hence which of the two forms can take more into solution, are illustrated further by Fig. 37, from various sources as indicated, where the diagrams for five systems with nepheline–carnegieite are superimposed. Note here that the

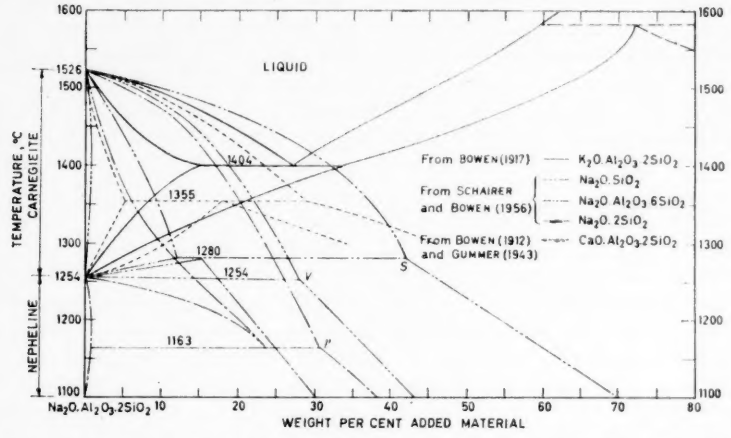

Fig. 37. Effect of various added materials on the inversion nepheline–carnegieite. (After various sources as indicated.)

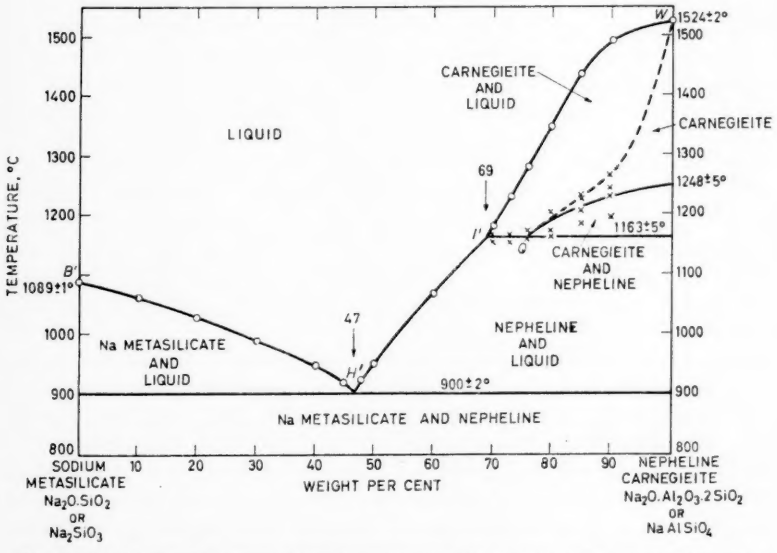

Fig. 38. Equilibrium diagram of the binary system $Na_2O \cdot SiO_2$ (sodium metasilicate)–$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ (nepheline, carnegieite) after TILLEY (1933), as given by SCHAIRER and BOWEN (1956). The value 900° ± 2° for the eutectic temperature is from SPIVAK (1944).

inversion temperature varies from 1163° (91° below) to 1404° (150° above) the inversion of the pure compound. The most unusual case is that of the system with $Na_2O \cdot SiO_2$; this is shown in its entirety as Fig. 38, from TILLEY (1933), and SPIVAK (1944), as given by SCHAIRER and BOWEN (1956). As the low-temperature phase takes less in solid solution, the inversion temperature is lowered. However, as a result of the large difference in the amounts of solid solution (24 per cent for carnegieite vs. essentially none for nepheline), it is possible to have a solid mass of carnegieite crystals of composition *Q* (Fig. 38), at 1163°, which will melt to form 20 per cent crystals of nepheline and 80 per cent liquid of composition *I'*, upon *cooling* one degree, to 1162°. Although this particular inversion may not take place in nature, carnegieite being unknown as a natural mineral, the phenomenon of melting of crystals upon cooling through an inversion may well occur in natural systems.

Incongruent Melting of Silicates

Before taking up the more complex quaternary and quinary systems, a few generalizations on the preceding diagrams should be made. It has long been known that certain silicates melt incongruently, i.e. upon heating they decompose to form another crystalline phase plus a liquid, neither of which has the same composition as the original silicate. The fact that this incongruent melting usually results in an enrichment in silica was pointed out by BOWEN (1928, particularly p. 298), who also discussed the consequences of this fact to igneous petrogenesis. As a number of new diagrams have been published since 1928, the following tabulation is presented.

Of the twenty-nine binary silicate compounds shown in LEVIN *et al.* (1956), twenty melt congruently, i.e. to a liquid of their own composition, and only nine melt incongruently. Eight of these nine melt to form a liquid more silica-rich than the original compound, but the amount of silica enrichment varies widely. Five yield liquids having only a fraction of a per cent to 3 per cent more silica than the original crystals, and one ($ZrSiO_4$) yields a liquid having approximately 50 per cent by weight silica over that of the crystals (LEVIN *et al.*, 1956, p. 67). In only one case does an incongruently melting binary compound yield a liquid poorer in silica than the original crystals. This is the compound $MnO \cdot SiO_2$, which melts to form crystals of silica and a liquid containing about 3 per cent less silica than the crystals (WHITE *et al.*, 1934; GLASSER and OSBORN, 1957). This is presumably a result of the region of liquid immiscibility in this system, which "pushes" the silica liquidus over the composition point of the metasilicate compound.

Of the sixty-eight ternary silicate compounds shown in the diagrams given in LEVIN *et al.* (1956), and the present paper, thirty-seven show congruent melting, and thirty-one melt incongruently. Of these thirty-one, only one—the compound sapphirine ($4MgO \cdot 5Al_2O_3 \cdot 2SiO_2$) in the system $MgO–Al_2O_3–SiO_2$—shows more than 10 per cent enrichment in silica in the liquid formed, and most of the rest show from zero to 5 per cent enrichment. Five of the thirty-one show slightly *less* silica in the liquid than in the original crystals. These five are as follows: $2Na_2O \cdot CaO \cdot 3SiO_2$ (MOREY and BOWEN, 1925), $Na_2O \cdot 2PbO \cdot 4SiO_2$ and $Na_2O \cdot 3PbO \cdot 7SiO_2$ (KRAKAU *et al.*, 1937, 1949), and $Na_2O \cdot 2MgO \cdot 6SiO_2$ and $Na_2O \cdot MgO \cdot 4SiO_2$ (SCHAIRER *et al.*, 1953). As these five have little petrologic significance, it can be said that Bowen's statement of thirty years ago is still

valid; in general, silicate compounds with incongruent melting points melt to form liquids richer in silica than the original crystals.

Any solid solution series actually represents an infinite series of incongruently melting compounds; although these have not been included above, they may have great significance in petrogenesis, as for example, the olivines, the pyroxenes and the plagioclases. In these the enrichment in the liquid on melting is toward higher iron and alkalies, rather than toward high silica.

In the above data, 31 per cent of the binary compounds melt incongruently, and 46 per cent of the ternary compounds melt incongruently, indicating an increase in incongruent character with increase in complexity of the compound. A crude parallel to this is found in the nature of the invariant points in binary, ternary and quaternary systems. In the systems described in this review, 22 per cent of the invariant points in binary systems, 51 per cent of the invariant points in ternary systems, and 72 per cent of the invariant points in quaternary systems are peritectics (reaction points), indicating a strong increase in peritectic behaviour with increasing complexity of the melt. Thus one might expect that peritectic relations will be the rule in natural, complex, magmas.

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Crystallization of Silica

BOWEN pointed out that, ". . . in spite of the high melting-point of silica, every dry system investigated in which SiO_2 is one of the components, whether the system is binary, ternary or quaternary, has shown free silica as one of the solid phases separating at the lowermost eutectic." (1928, p. 298.) As shown above, the additional diagrams that have been determined still bear out this statement, if it is changed to read "one of the lowermost eutectics."

One interesting aspect of these systems is the size and shape of the field of silica on the various diagrams. The boundary of the field of the various silica minerals, in each of the fifteen different ternary oxide systems described above, has been sketched in Fig. 39. Minor differences, as between the metastable tridymite and stable quartz boundary curves, have been ignored. Although it is obvious that the terminations of the boundary curves are controlled by equilibria in the individual binary systems, it is equally obvious that these boundary curves could not be determined by simple interpolation from the limiting binary systems. The five systems with Al_2O_3 all show a similar rapid increase in the Al_2O_3–SiO_2 ratio of liquids along the boundary line originating at the Al_2O_3–SiO_2 eutectic, with increasing amounts of the third component; the system Na_2O–Fe_2O_3–SiO_2 apparently shows a similar behaviour with respect to Fe_2O_3, although the extrapolations to this sideline from the data on the systems Na_2O–Fe_2O_3–SiO_2 (BOWEN *et al.*, 1930) and FeO–Fe_2O_3–SiO_2 (MUAN, 1955) do not agree (see Figs. 21 and 30). The shape of the silica boundary curve, and particularly its position near the centre line of the triangle (Fig. 39) are strongly affected by the composition of the most siliceous ternary compound in the system. Thus six of the seven systems whose silica boundary curves cross below point *X* on Fig. 39 have, for their most siliceous ternary compounds, ratios of Si/O ranging from 1/3·0 to 1/4·0, whereas the eight that cross above point *X* have for their most siliceous ternary compounds, ratios of Si/O ranging from 1/3·0 to 1/2·33. One system, (MgO–FeO–SiO_2), whose boundary also crosses below point *X*, has no ternary compound as such. Other factors must also be involved in the explanation of these boundary curves, however. Thus in

the system K_2O–MgO–SiO_2 (Fig. 25), the field for the binary compound protoenstatite extends considerably further toward the SiO_2 apex (up to approximately 83 per cent SiO_2) than the fields of any of the ternary compounds in this or other systems (see Fig. 39).

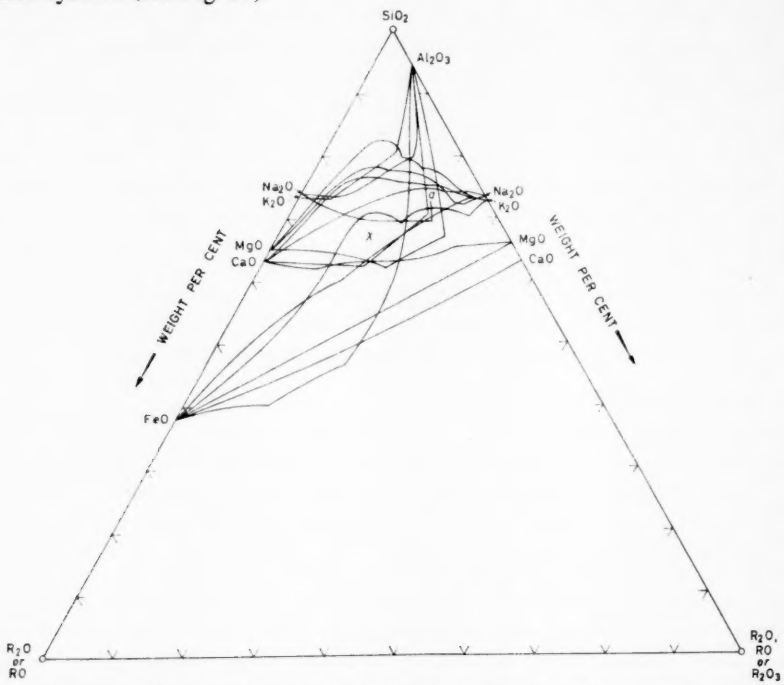

Fig. 39. Boundary curves limiting the field of the silica minerals in various systems, from various references as given in text. Each individual line represents the limits of the fields of the silica minerals, quartz, tridymite, and cristobalite, in the system between SiO_2 and the two oxides named at the ends of the line. The line ending at *a* is for the system Na_2O–Fe_2O_3–SiO_2; its termination on the binary system Fe_2O_3–SiO_2 is not known.

Ternary Subsystems from Four- and Five-component Oxide Systems

As mentioned above, the fact that a comparatively few minerals make up the bulk of igneous rocks makes it possible to choose very limited portions of four- and five-component systems which will, however, closely approach the ranges of igneous rock composition. Thus the very complex five-component system K_2O–CaO–MgO–Al_2O_3–SiO_2 has not been worked out, but the relatively simple system diopside–potassium feldspar represents a petrologically significant "binary" system in the quinary system. The following pages show twelve of the petrologically most significant subsystems containing four and five oxides from the general system K_2O–Na_2O–CaO–FeO–MgO–Fe_2O_3–Al_2O_3–SiO_2. These all have as their components, or as intermediate compounds, the following common rock-forming minerals in addition to silica:*

* There are many combinations of these minerals that can be found as subsystems in the ternary-oxide systems described above. Thus the classic system forsterite–diopside–silica (BOWEN, 1914) falls in the system CaO–MgO–SiO_2 (Fig. 18).

Olivines—Forsterite and fayalite
Pyroxenes—Diopside, enstatite (including clinoenstatite and protoenstatite) and the pyroxenoid wollastonite (and pseudowollastonite)
Feldspars—Anorthite, albite and "orthoclase" (potassium feldspar)
Feldspathoids—Leucite, nepheline, "K-nepheline" (kaliophilite and kalsilite).

One of the most important features of the interrelationships of these rock-forming minerals in silicate melts is the trend in composition of the liquids,

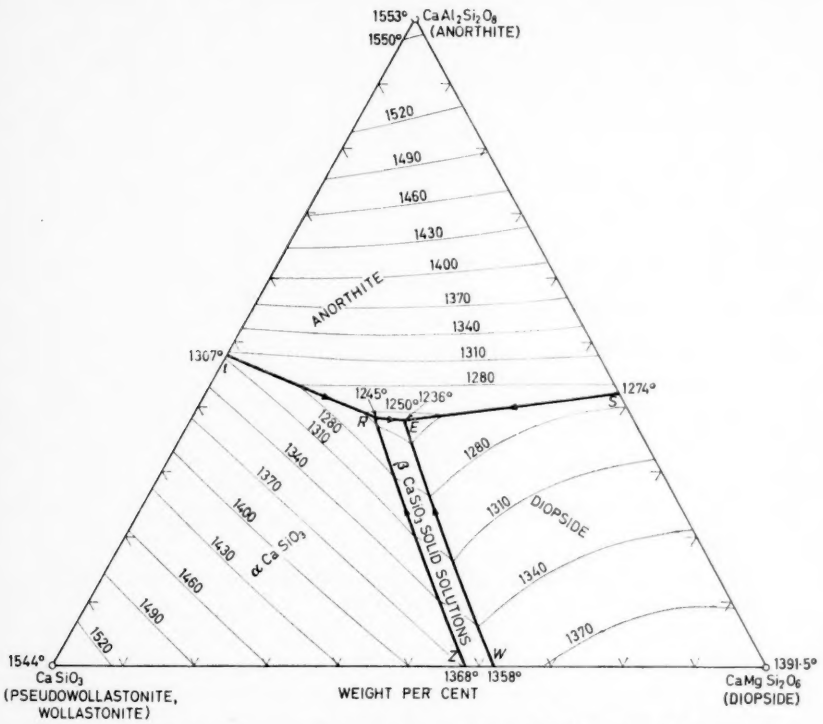

Fig. 40. Equilibrium diagram of the system pseudowollastonite–diopside–anorthite. (After OSBORN.)

with either normal equilibrium crystallization, or particularly with the geologically inevitable crystal fractionation, toward low-melting eutectic liquids rich in alkali aluminosilicates and silica, extremely poor in CaO, MgO, Fe_2O_3, Al_2O_3 over a 1:1 ratio with total alkalis, and to a lesser degree, poor in FeO. This trend was very apparent in some of the systems described above, such as Na_2O–CaO–SiO_2 (Fig. 24), but becomes even more apparent in the diagrams of the various systems between the above rock-forming minerals.

Pseudowollastonite–Diopside–Anorthite ($CaO \cdot SiO_2$–$CaO \cdot MgO \cdot 2SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$). The liquidus phase diagram for this system is given in Fig. 40, from OSBORN (1942). It is apparent from this diagram that although there is a decided lowering of the eutectic below the melting points of the components, the final eutectic *E*, between anorthite, wollastonite solid solution ($\beta CaO \cdot SiO_2$

with Mg) and diopside (slightly aluminous) lies practically in the middle of the diagram, and occurs at a relatively high temperature (1236°).

Anorthite–Forsterite–Silica ($CaO \cdot Al_2O_3 \cdot 2SiO_2$–$2MgO \cdot SiO_2$–$SiO_2$). This system, also from the quaternary CaO–MgO–Al_2O_3–SiO_2, is similar to the foregoing one in that no alkali is present, and temperatures, even at the lowest eutectic, are relatively high. The diagram for this system (Fig. 41) was one of the

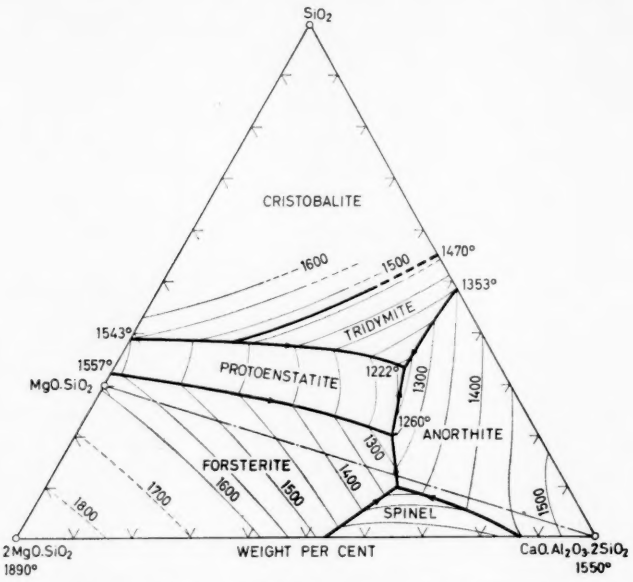

Fig. 41. Equilibrium diagram of the system anorthite–forsterite–silica. (After ANDERSEN.)

rather early products of the Geophysical Laboratory, having been published by ANDERSEN in 1915. It shows the incongruent melting of $MgO \cdot SiO_2$, yielding a reaction line from 1557° to the ternary reaction point or peritectic at 1260°, which has been a pedagogical stand-by for countless professors of petrology. Another interesting feature of the system is the field of spinel, representing non-ternary (quaternary) equilibrium, as the composition of spinel cannot be represented in terms of the three components. Forsterite and anorthite cannot coexist, with liquid, in binary mixtures of the two, as they will react to form spinel. However, if there is excess silica present in the liquid (i.e. the composition lies inside the triangle), these two phases can coexist with liquid.

Anorthite–Leucite–Silica ($CaO \cdot Al_2O_3 \cdot 2SiO_2$–$K_2O \cdot Al_2O_3 \cdot 4SiO_2$–$SiO_2$). This system is shown in Fig. 42, from SCHAIRER and BOWEN (1947a). It is readily apparent that the lowest-melting liquid in this system, point *V*, is essentially the eutectic mixture of potash feldspar and silica, point *U*, with very little added anorthite. Conversely, anorthite can be said to be highly insoluble in potash feldspar–silica melts, except at elevated temperatures. The incongruent melting of potash feldspar to form leucite plus liquid is also readily visible.

Anorthite–Nepheline–Silica ($CaO \cdot Al_2O_3 \cdot 2SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$–$SiO_2$). A preliminary diagram for this system from SCHAIRER (1957) is shown in Fig. 43. There are two low-melting liquids in this system, at 1062° and 1068°, on either side of albite along the nepheline–silica sideline. All crystallization trends toward these two points. The large "plagioclase" field across the centre of the diagram represents the solid solution series between anorthite and albite. The

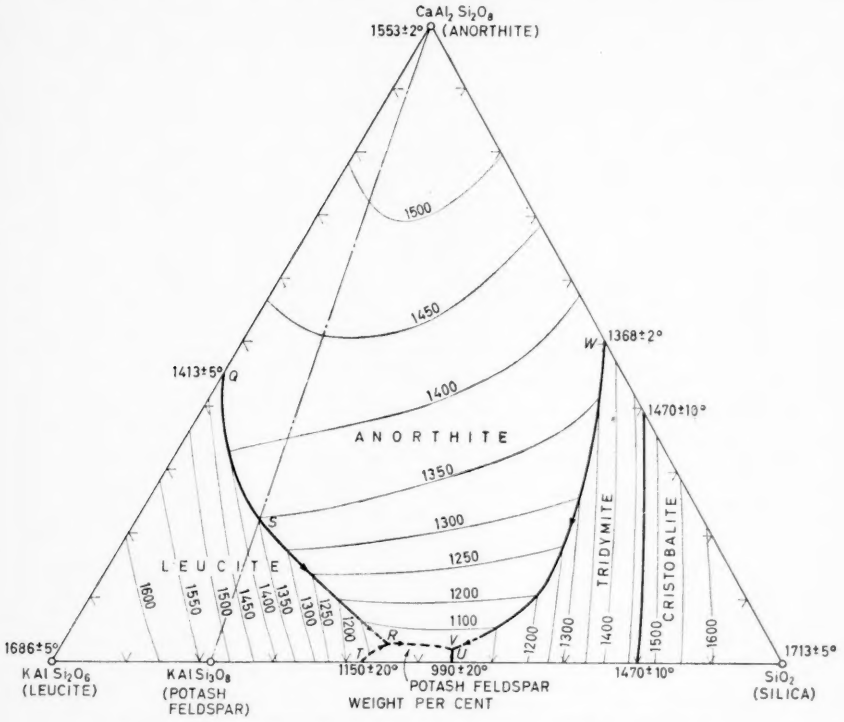

Fig. 42. Equilibrium diagram of the system anorthite–leucite–silica. (After SCHAIRER and BOWEN.)

field for alumina represents quaternary equilibria in the more general system Na_2O–CaO–Al_2O_3–SiO_2.

Anorthite–Potassium Feldspar–Sodium Feldspar ($CaO \cdot Al_2O_3 \cdot 2SiO_2$–$K_2O \cdot Al_2O_3 \cdot 6SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$). This system, shown in Fig. 44, was determined by FRANCO and SCHAIRER (1951). It appears to be a simple ternary solid solution series, at liquidus temperatures, with the exception of the potassium feldspar corner, where the incongruent melting of this material results in a field of leucite. As leucite is a very low density phase, this incongruent melting is eliminated by adequate pressure, further simplifying the system. Below the liquidus, however, this system is far from simple, and as this system and the quaternary one between the three feldspars and silica have very great petrologic significance, considerable effort is being put into unravelling the intricacies of the three feldspars,

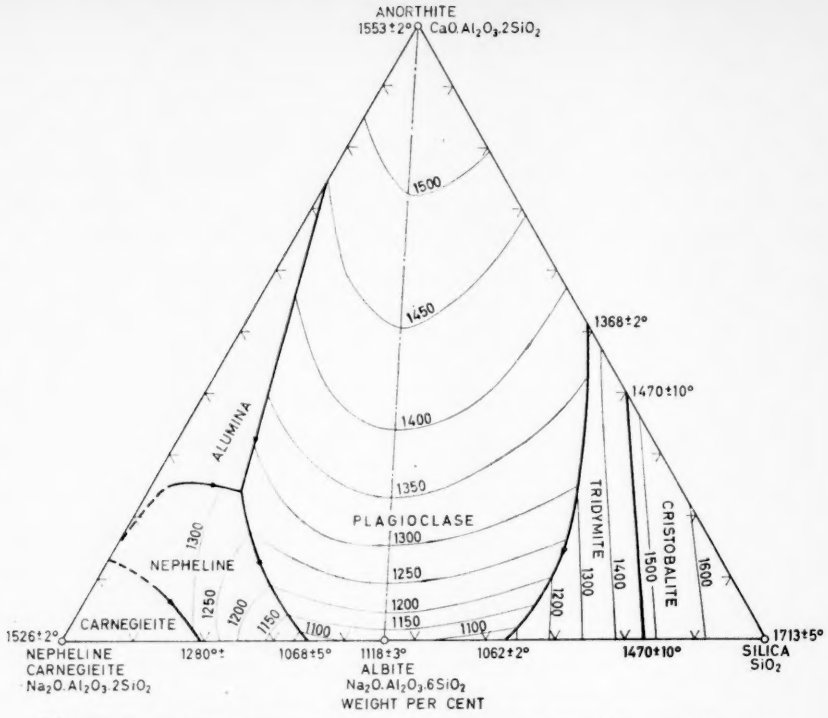

Fig. 43. Preliminary equilibrium diagram of the system anorthite–nepheline–silica. (After SCHAIRER.)

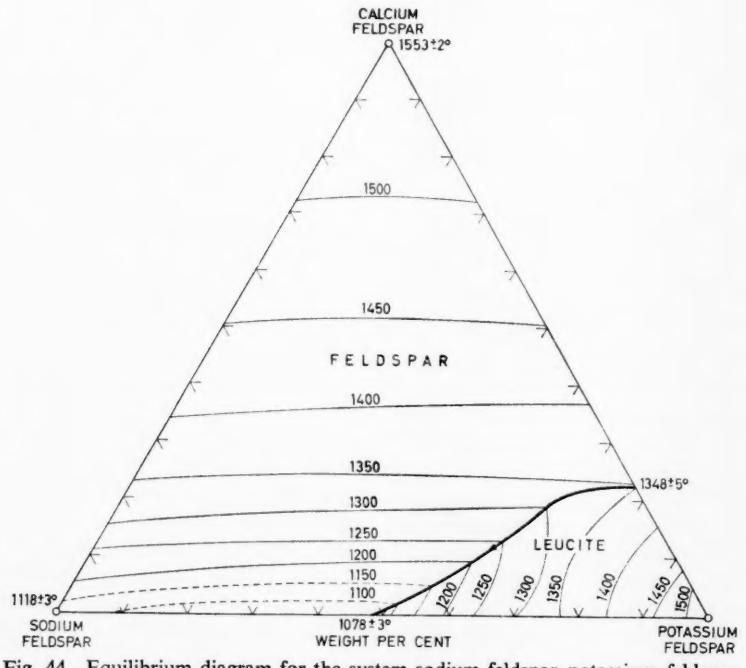

Fig. 44. Equilibrium diagram for the system sodium feldspar–potassium feldspar–calcium feldspar. (After FRANCO and SCHAIRER.)

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their modifications, solid solution limits and equilibria, particularly under hydrothermal conditions.

Diopside–Leucite–Silica ($CaO \cdot MgO \cdot 2SiO_2$–$K_2O \cdot Al_2O_3 \cdot 4SiO_2$–$SiO_2$). This diagram, published by SCHAIRER and BOWEN (1938), is reproduced in Fig. 45. The very flat field of diopside, extending practically to the potassium feldspar–silica sideline, attests to the insolubility of diopside in such melts. The low

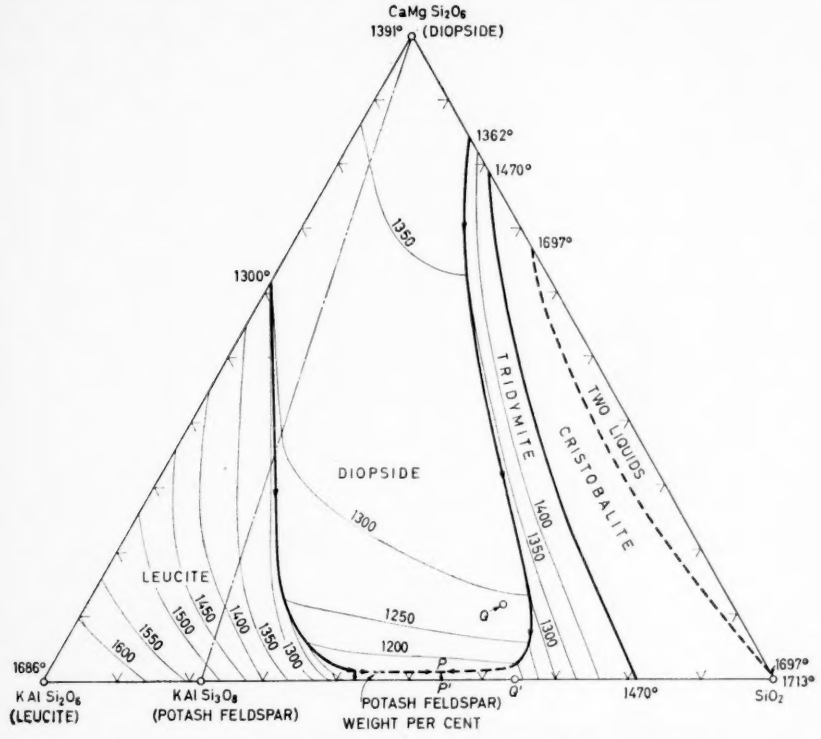

Fig. 45. Equilibrium diagram of the system diopside–leucite–silica. (After SCHAIRER and BOWEN.)

slope of this liquidus becomes particularly apparent when a point such as Q is considered. This point, consisting of 12 per cent diopside, 88 per cent mixture Q', has a diopside liquidus only 100° lower than pure diopside. The lowest-melting liquid is at point P, and consists essentially of the potassium feldspar–silica eutectic liquid P', with an unknown but necessarily very small amount of diopside.

Diopside–Nepheline–Silica ($CaO \cdot MgO \cdot 2SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$–$SiO_2$). The diagram for this system, as determined by Schairer, was first given by YODER (1950, p. 318), and is reproduced here as Fig. 46. It shows that diopside is rather insoluble in albite–silica melts, the lowest-melting liquid from which diopside can crystallize being at 1075°, and only a few per cent diopside. The system nepheline–diopside is not binary, in that forsterite appears on it, and the field that normally would be for albite alone is instead a field for plagioclase, i.e.

melts in this portion of the system crystallize a feldspar containing some calcium, and the equilibria are quaternary, not ternary.

Diopside–Albite–Anorthite ($CaO \cdot MgO \cdot 2SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$). This system, a ternary plane through the more general quinary system, Na_2O–CaO–MgO–Al_2O_3–SiO_2, was the first ternary system to be studied that approached igneous rock compositions rather closely. The diagram,

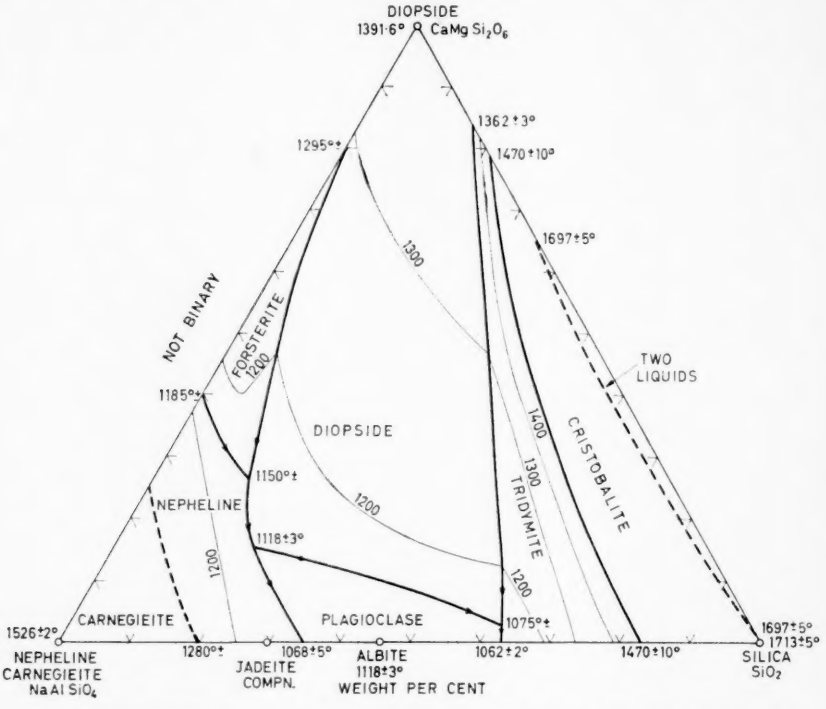

Fig. 46. Equilibrium diagram of the system diopside–nepheline–silica. (After SCHAIRER.)

which is surprisingly simple considering its significance, is shown in Fig. 47, after BOWEN (1915). Each point on the boundary line between the two fields represents a liquid in equilibrium with diopside and a plagioclase. Thus liquid *a* is in equilibrium with diopside *d* and plagioclase *b*, as shown by the three phase triangle *abd*. The composition of the crystals forming from liquid *a* (i.e. the gross composition of the material being extracted from the liquid by crystallization and by reaction), must lie along the tangent to the boundary line at *a*. The manner in which the position and shape of these three phase triangles controls the crystallization paths in a system including a solid solution has been discussed by OSBORN and SCHAIRER (1941) for the system pseudowollastonite–akermanite–gehlenite.

As pointed out above, compositions in the system diopside–albite–anorthite are such that they approach that of basalt. Thus a mixture of composition *G* (Fig. 47), consists of diopside, 40 per cent, and labradorite (An_{50}), 60 per cent.

This composition is not far removed from that of the average Deccan trap (BOWEN, 1928, p. 66), particularly if some Fe is substituted for the Mg in the pyroxene, a change which should have relatively little effect on this equilibrium. One important feature of such compositions is that upon cooling they become saturated with respect to plagioclase and pyroxene simultaneously, as Bowen

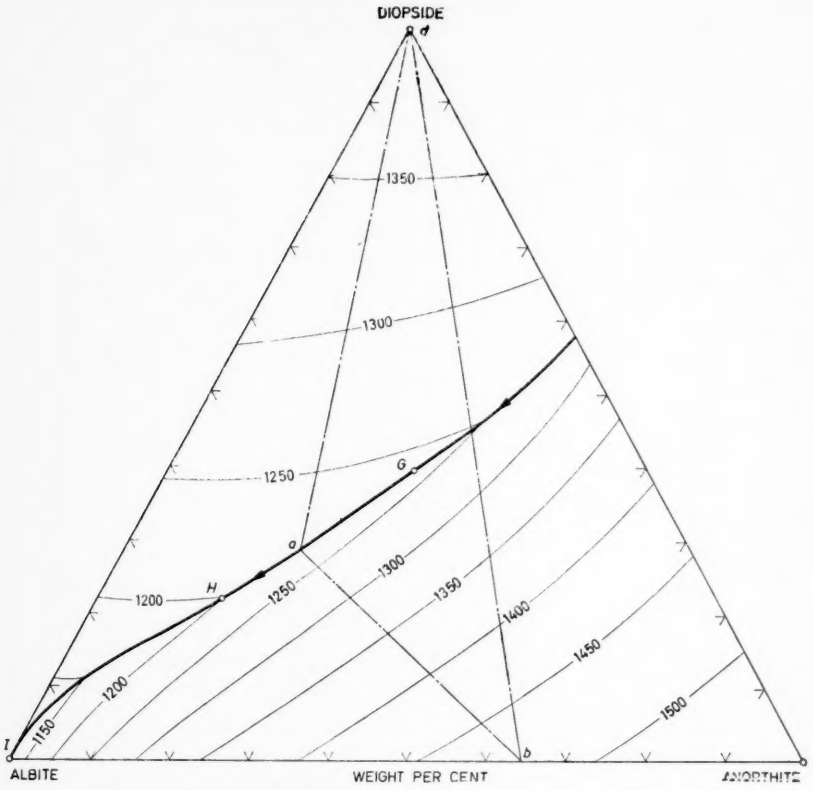

Fig. 47. Equilibrium diagram of the system diopside–albite–anorthite, with isotherms and one three phase triangle. (After BOWEN.)

has pointed out is characteristic of natural basaltic liquids. Another interesting feature is the short range of temperature between liquidus and solidus for such compositions. Mixture *G*, for example, starts forming crystals of pyroxene and plagioclase (about An_{80}), at about 1240°, and at equilibrium the last liquid, having composition *H*, solidifies only 40° lower (at about 1200°). This equilibrium crystallization behaviour is illustrated by the solid lines on Fig. 48. With crystal fractionation, as by the settling of crystals, the crystallization range is increased considerably, but is still rather narrow (155°), and the last liquid, at 1085°, has the composition *I* (Fig. 47), consisting of albite plus a very little diopside, as the diagram was drawn by Bowen in 1915. Point *I*, which could only be estimated by Bowen, due to the high viscosities, probably should be placed at a

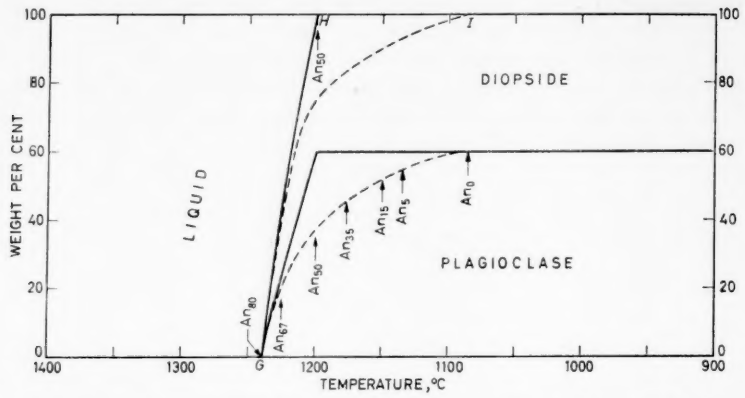

Fig. 48. Diagram showing the phases present at equilibrium (solid lines) in a mixture of composition *G* (Fig. 47). The dashed lines show the behaviour of the same composition under conditions of crystal fractionation.

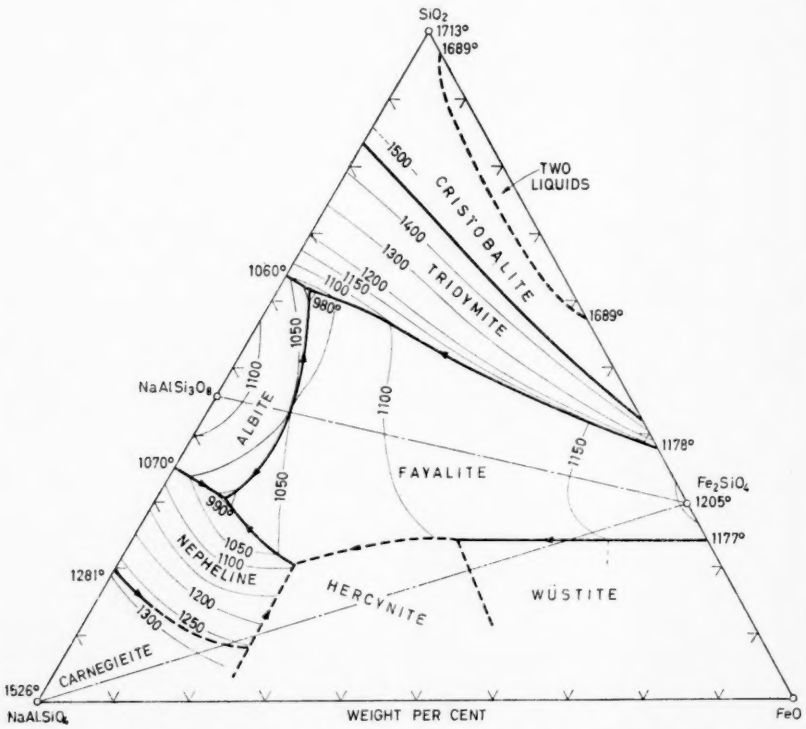

Fig. 49. Equilibrium diagram of a part of the system nepheline–FeO–SiO_2, showing the relations between nepheline, albite, and fayalite. (After BOWEN and SCHAIRER.)

somewhat higher per cent diopside (see Fig. 46); the actual relations in this area, though of great importance, are not yet thoroughly understood. On Fig. 48 the dashed lines correspond to crystallization with crystal fractionation (i.e. non-equilibrium), calculated by assuming that 10 per cent of the residual liquid from the previous step crystallizes, and the crystals are separated, at each of a series of steps. Note that even in this case, the bulk of the liquid crystallizes

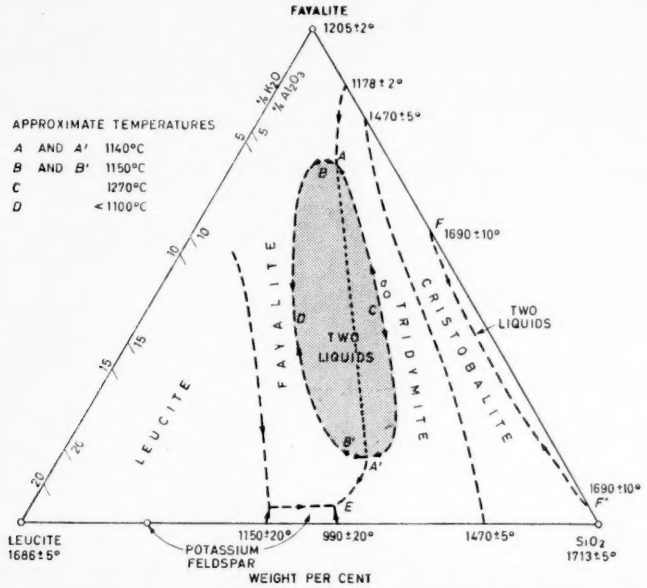

Fig. 50. Preliminary equilibrium diagram for the system fayalite–leucite–silica, showing the fields of the several crystalline phases and the intersection of the new area of immiscibility with the liquidus surface (shaded). In the area $AA'CA$ two liquids are in equilibrium with silica crystals, and in the area $AA'B'DBA$ two liquids are in equilibrium with fayalite crystals. Along the line AA' two liquids (A and A') are in equilibrium with each other and with crystals of both silica and fayalite. The tie line between conjugate liquids B' and B, extended, goes through the composition point for fayalite, making this line a true binary system and the points B and B' a maximum on the line $ABDB'A'$. All melts contain Fe_2O_3 in amounts representing equilibrium with pure metallic iron. (After ROEDDER.)

in the first 50 degrees drop in temperature below the liquidus. The differences between the results with and without fractionation have been discussed in detail for another system (OSBORN and SCHAIRER, 1941), but are equally applicable here.

Fayalite–Nepheline–Silica ($2FeO \cdot SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$–$SiO_2$). The phase diagram for this system, as presented by BOWEN and SCHAIRER (1938), is given in Fig. 49, where it is plotted as a subsystem in the system FeO–nepheline–SiO_2. Although fayalite is a low-melting compound (m.p.–1205°) it is still relatively insoluble in alkali–aluminosilicate melts, as shown by the positions of the two eutectics, near to the composition of albite. The eutectic with silica, fayalite, and albite at 980° corresponds roughly to a fayalite soda-granite, with about 6 per cent fayalite.

Fayalite–Leucite–Silica ($2FeO \cdot SiO_2$–$K_2O \cdot Al_2O_3 \cdot 4SiO_2$–$SiO_2$). A preliminary diagram of this system, after ROEDDER (1951b), is given in Fig. 50. This system is interesting in that it shows that fayalite is relatively insoluble in potash feldspar–silica melts. Point *E* has not been determined accurately, but can hardly contain more than a few per cent fayalite, and may contain much less. The liquidus on the fayalite field in this system has a strong inverse curvature, and one portion is actually isothermal over a range of compositions, i.e. liquid immiscibility is involved. This immiscibility occurs at considerably lower temperatures (to less than 1100°C), and considerably higher alkali and alumina contents (to over 16 per cent $K_2O + Al_2O_3$), than in all other silicate systems showing immiscibility. The area in which this low temperature immiscibility intersects the liquidus surface in this system is shaded in Fig. 50, and overlies the boundary curve for the fields of fayalite and silica, yielding very unusual

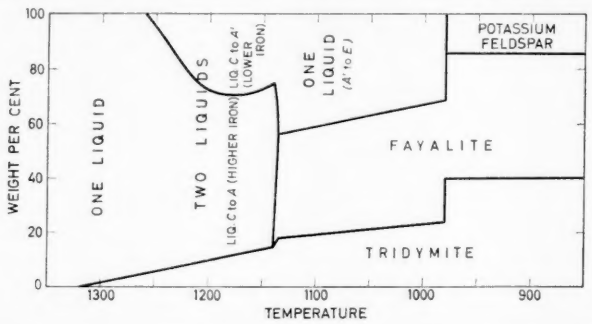

Fig. 51. Diagram showing the phases present, at equilibrium, in a mixture of composition *a*, Fig. 50 (leucite 14, fayalite 46, silica 40). The phase change at 1140° is shown to take place over an assumed small temperature interval, as there is some Fe_2O_3 present in these liquids, precluding truly invariant conditions when four phases are present. This interval has not been measured experimentally.

crystallization histories (see Fig. 51). This area represents a section through a two-liquid immiscibility phase volume in the system K_2O–FeO–Al_2O_3–SiO_2, the general shape of which has been determined (ROEDDER, 1953) but the full data have not been published. There is some evidence that the low temperature immiscible liquid field in the system fayalite–leucite–silica is connected, metastably under the silica liquidus surface, with the high temperature two liquid field along the fayalite–silica sideline, and also that it extends, metastably, under the practically flat fayalite field. This introduces the problems of the possible presence of a field of two immiscible liquids in various other systems showing practically flat and even inverse curvatures to the field for some phase. This region of immiscibility can either occur, stably, just above the liquidus, or else it can occur, metastably, just beneath the liquidus. In either case there will be a similar, nearly flat portion on the liquidus surface. Among the systems presented in this review, this type of liquidus is approached mostly in combinations of a silicate containing a divalent element (Ca, Mg, Fe), with alkali–aluminosilicate mixtures approaching the composition of the eutectics sodium feldspar–silica, and potassium feldspar–silica. Several of these binary and semi-binary systems are sketched in Fig. 52, as plotted graphically from the various

sources given above. The existence of a low two-liquid "dome," cutting the liquidus *from below*, in the system fayalite–(potash feldspar–silica), would suggest that the reverse curvature in the system fayalite–(albite–silica), and perhaps the shape of some of the other liquidus curves, may reflect fields of immiscibility occurring metastably below the liquidus.

Forsterite–Leucite–Silica ($2MgO \cdot SiO_2$–$K_2O \cdot Al_2O_3 \cdot 4SiO_2$–$SiO_2$). This system

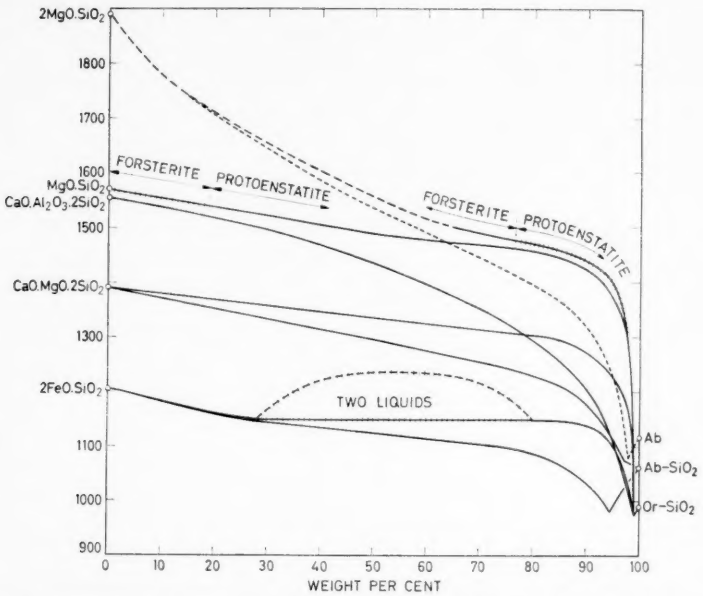

Fig. 52. Composite diagram showing the binary systems between a series of silicates of divalent ions (forsterite, "enstatite" ($MgO \cdot SiO_2$), anorthite, diopside and fayalite), and alkali–aluminosilicate liquids of the eutectic composition potassium feldspar–silica ("Or–SiO_2", point *I* in Fig. 34) and sodium feldspar–silica ("Ab–SiO_2", point *I* in Fig. 35). All of these curves represent binary equilibria except for the portions cross hatched. All have been sketched by graphical methods, from the appropriate ternary systems given above, except the dotted line for the system forsterite–albite, which represents unpublished data furnished through the courtesy of Mr. Robert Insley.

was studied by SCHAIRER (1954) as one of the ternary planes in the general system K_2O–MgO–Al_2O_3–SiO_2 (see Fig. 58). The phase diagram for this ternary, as given by SCHAIRER (1957), is shown in Fig. 53. The potash feldspar field is vanishingly small in this system—only 0·2 per cent by weight forsterite results in the elimination of feldspar as the primary phase, i.e. magnesium silicates are exceedingly insoluble in these liquids. (The analogous system with nepheline in place of leucite has been studied by Greig at the Geophysical Laboratory, but the results have not been published.) The strong curvature of the boundary line between the fields of protoenstatite and silica, and the very small slope to the upper part of the protoenstatite liquidus surface results in very unusual crystallization histories, two of which are shown in Figs. 54 and 55, for

compositions *A* and *B* in the protoenstatite field of Fig. 53. Although both of these compositions are made of the same three materials, and there is comparatively little difference in the temperature of their protoenstatite liquidus, their general behaviours on crystallization are diametrically opposite. If magmas such as these occurred in nature, it is obvious that phenomena resulting from the formation and distribution of pyroxene phenocrysts should be quite different in the two cases.

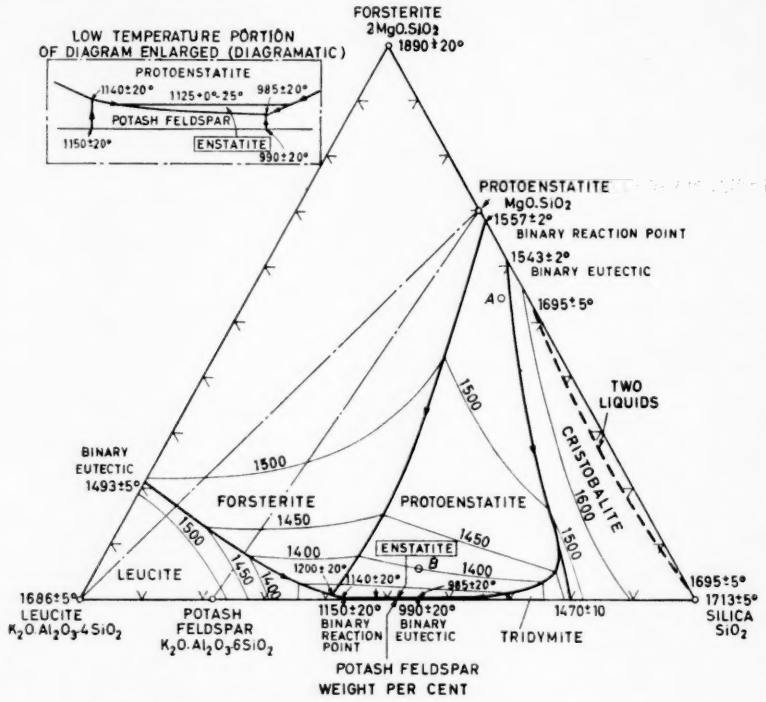

Fig. 53. Equilibrium diagram of the system forsterite–leucite–silica. (After SCHAIRER.)

Potash Nepheline–Nepheline–Silica ($K_2O \cdot Al_2O_3 \cdot 2SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$–$SiO_2$). Although no one has attempted a rigorous laboratory approach to the eight-component system K_2O–Na_2O–CaO–FeO–MgO–Fe_2O_3–Al_2O_3–SiO_2, for the reasons discussed earlier, it is obvious from the numerous possible 3-, 4- and 5-component systems, and in particular from the specific subsystems discussed above, that there are certain crystallization trends in common, which may logically be assumed to occur in mixtures of all eight components. In all of the subsystems discussed above, the general crystallization trends, for liquids resembling igneous rocks in composition, are toward the crystallization of phases that will deplete the melt of most of its CaO, MgO, Fe_2O_3, and most of the Al_2O_3 molecularly in excess of the amount of alkalis present. This yields a net enrichment in K_2O, Na_2O and FeO, and usually in Al_2O_3 and SiO_2 as well.

Further crystallization results in the depletion of even the FeO, so that the residual liquids from this process will be essentially compositions in the system K_2O–Na_2O–Al_2O_3–SiO_2. Obviously, the reverse process of selective fusion of a polycomponent mixture of these oxides will give similar liquids, in the reverse order, except for any effects specifically caused by disequilibrium on cooling. Although some phenomena resulting from disequilibrium on cooling may be

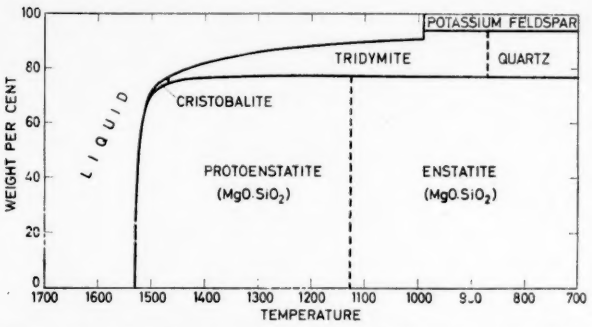

Fig. 54. Diagram showing the phases present, at equilibrium, in a mixture of composition *A*, Fig. 53. Note that 72 per cent of the melt crystallizes in the first 30° drop from the liquidus, but that the remaining liquid does not crystallize completely until 510° lower.

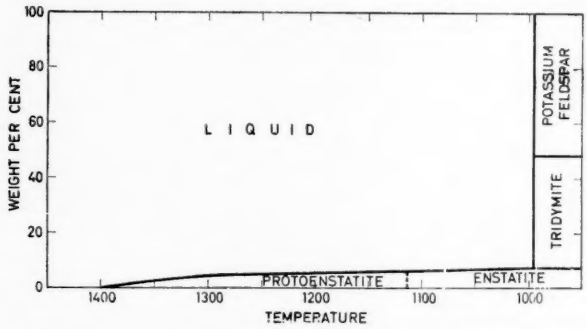

Fig. 55. Diagram showing the phases present, at equilibrium, in a mixture of composition *B*, Fig. 53. Note that although this point falls in the same field as point *A* (Fig. 52), only 7·5 per cent is solid at 990°, 410° below the liquidus.

reversed on heating, this is not necessarily true, particularly where there has been a physical separation of phases. Reaction with inclusions of wall rocks, as discussed by BOWEN (1922) represents in effect a reversal of the equilibria on cooling.

As most igneous rocks that even approach the system K_2O–Na_2O–Al_2O_3–SiO_2 in composition are at least 50 per cent SiO_2, and have the sum of $K_2O + Na_2O$ approximately equal to Al_2O_3, (on a molecular basis), the section $K_2O \cdot Al_2O_3 \cdot 2SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$–$SiO_2$ through this quaternary system should come close to representing their compositions. This system was very aptly termed "petrogeny's residua system" by BOWEN (1937), as it represents the goal for

the compositions of the residual liquids, not only in the synthetic systems, but also in the natural systems, wherever evidence of natural residual liquids is available.

Wherever the evidence permits evaluation of the sequence of crystallization, the rocks show that the oxide ores, olivines, pyroxenes and calcic plagioclase separate early and almost quantitatively from magmas (i.e. they become highly insoluble under lowered temperatures), eventually resulting in low-melting,

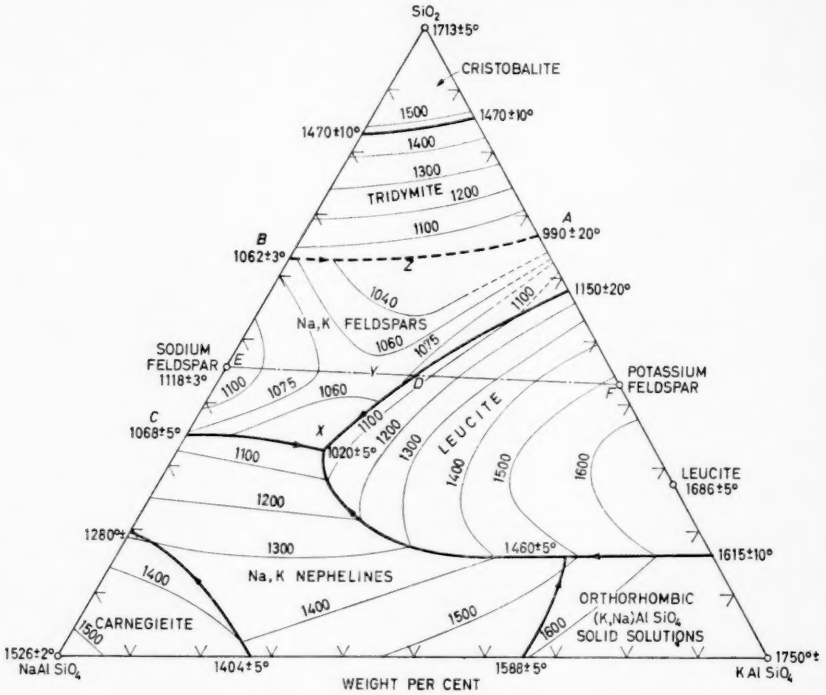

Fig. 56. Revised equilibrium diagram of the system $K_2O \cdot Al_2O_3 \cdot 2SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$–$SiO_2$. (After SCHAIRER and BOWEN.)

liquid alkali–aluminosilicate residua. This will take place under conditions of equilibrium crystallization, and even more so under conditions of fractional crystallization, although there are some differences of opinion as to the *specific* results of fractional crystallization.

The diagram for the system $K_2O \cdot Al_2O_3 \cdot 2SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$–$SiO_2$ was first given by SCHAIRER and BOWEN (1935), and later was given in a revised form, as shown in Fig. 56, by SCHAIRER (1950). It is apparent that the last residual liquids in most of the systems discussed above, neglecting relatively insignificant amounts of silicates of Ca, Mg and Fe, would fall on the sidelines of this system, in the vicinity of the binary eutectics of the feldspars with silica (points *A* and *B*) or in a few cases at the eutectic with nepheline (point *C*). Mixtures containing both potassium and sodium can be expected to fall in the area between these points. One can think of rock magmas as multicomponent systems, plotted in

polydimensional space above this diagram, which simplify themselves, by quantitative crystallization of various components, until they finally come funnelling out of polydimensional space to land in this ternary system. Regardless of where they start in this system, however, the results will be similar. The residual liquid compositions for *this* system lie in a saddle-like trough of low liquidus temperatures, centered about the points *X*, *Y* and *Z*, and thus corresponding in composition to leucocratic nepheline syenite, syenite and granite, respectively, or to their effusive equivalents. Crystallization paths in the feldspar field are strongly curved as a consequence of the solid solution series with a

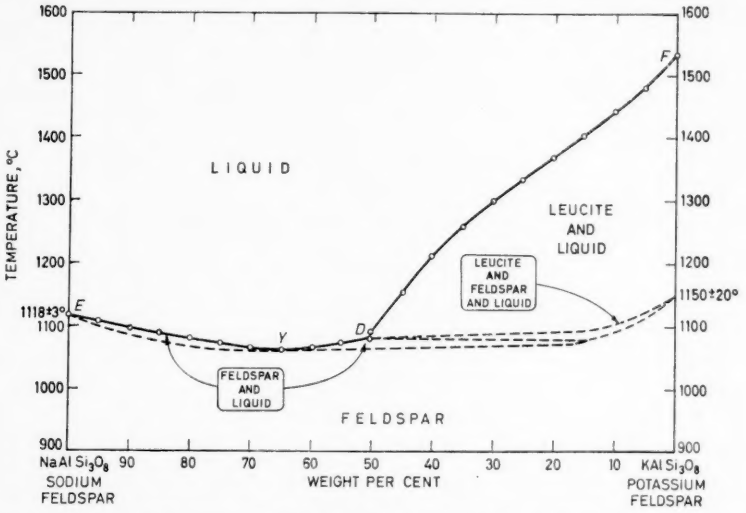

Fig. 57. The alkali–feldspar join $K_2O \cdot Al_2O_3 \cdot 6SiO_2$–$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$. Heavy solid or dashed curves refer to binary equilibrium. Light solid or dashed curves refer to ternary equilibrium. Open circles indicate determined points. (After SCHAIRER.)

minimum between albite and orthoclase (shown in Fig. 57 from SCHAIRER, 1950). There has been an intensive study of these crystallization paths, under various water pressures, in order to understand the derivation of granitic and rhyolitic magmas (for example TUTTLE, 1955).

Throughout this process, there has been an ever-increasing amount of water, carbon dioxide, and various trace elements including sulphur and the ore elements, in the residual liquid, as small amounts of all of these materials are present in the original magma, and as the bulk of the phases that can form under the conditions that must obtain up to this point, both in the laboratory and the earth, are free of these materials. The behaviour of trace elements during magmatic differentiation has been discussed by numerous writers, and has been summarized by OSBORN (1950). Other than the occasional formation of small amounts of early hornblende and biotite in some rocks, and the general lowering of the liquidus, these components have had very little effect on the equilibria up to this point, and the phase equilibria for the anhydrous systems represent a reasonably close approach to the actual conditions. Further crystallization of the anhydrous phases in this system results in still greater concentration of

water (and other materials) into the residual liquid, however, and from here on these residual liquids behave in a manner controlled more by these volatile materials than by the non-volatile components. (See ROY and TUTTLE, 1956, volume 1 of this series.)

Other Systems of Petrological Interest

Many other systems of petrological interest have been studied, only a few of which can be mentioned here. In particular, many other ternary or partially

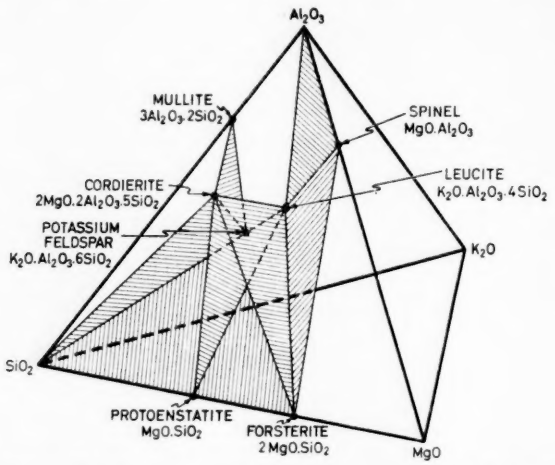

Fig. 58. Diagram showing seven of the ternary planes through the general system K_2O–MgO–Al_2O_3–SiO_3 that have been investigated by SCHAIRER.

ternary planes through the tetrahedrons representing four-component systems have been reported in the literature. Much of this work was done for its pertinence to industrial problems involving slags, cements and refractories (see LEVIN *et al.*, 1956). The four systems in which the most work of petrological significance has been done are the four-component systems combining Al_2O_3 and SiO_2 with K_2O + MgO (see below), Na_2O + CaO (see GREENE and BOGUE, 1946; GOLDSMITH, 1947), CaO + FeO (see SCHAIRER, 1942; MUAN and OSBORN, 1951), and CaO + MgO (see OSBORN and TAIT, 1954; DEVRIES and OSBORN, 1957). Extensive studies have also been made in the system MgO–FeO–Fe_2O_3–SiO_2 (MUAN and OSBORN, 1956). Although several dozen ternary or partially ternary planes in the first four systems alone have been studied and published in recent years, and smaller portions of many other systems have been studied, only one of the systems can be given here as an illustration.

The system K_2O–MgO–Al_2O_3–SiO_2 was studied by SCHAIRER (1954, 1955). Three of the four limiting ternary systems making the faces of the tetrahedron representing this system had been studied previously (see above) and as most of the interest lay in the higher silica mixtures, the fourth ternary K_2O–MgO–Al_2O_3, was not studied. A number of binary and ternary compounds were known, and these were chosen as the components for a series of seven 3-component systems

published by SCHAIRER (see Fig. 58), and data have been obtained but are yet to be published on a large number of additional triangular joins in the system, connecting these and other compounds (SCHAIRER, 1955, 1957). One of these seven joins, the system forsterite–leucite–silica, has been presented above as Fig. 53.

A study of this type is aimed at understanding the mutual relationships of the various phases in the system, the trends taken by liquids upon crystallization, and the temperatures involved, and at providing the necessary base for experiment or extrapolation into more complex systems, in this particular instance

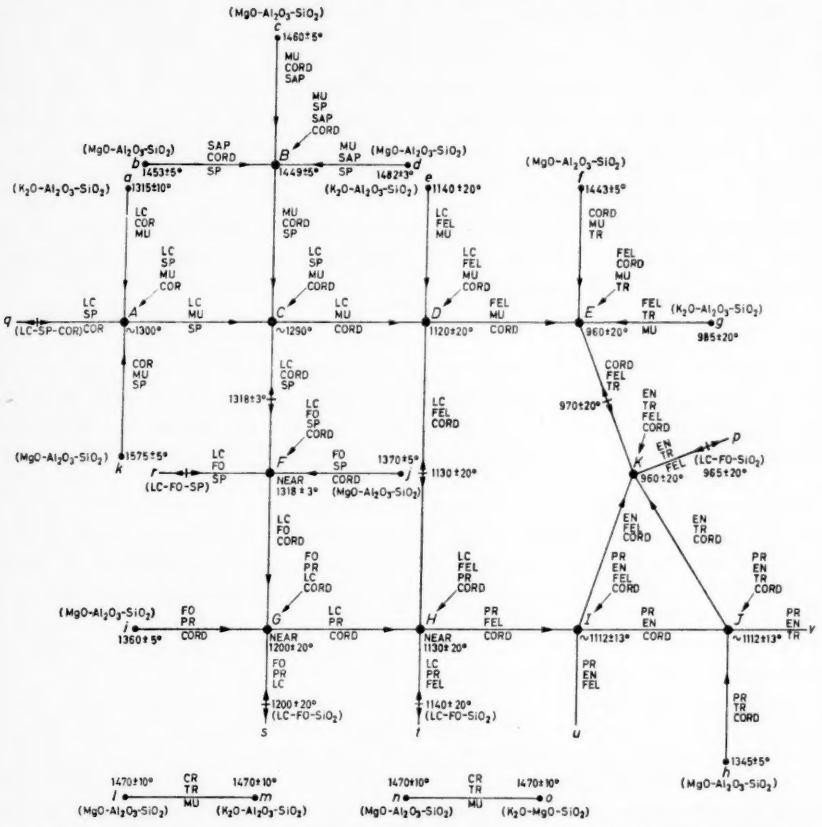

Fig. 59. Diagram showing univariant lines and their relation to ternary invariant points (small black dots and letters a through o) in limiting systems and to quaternary invariant points (large black dots and capital letters). All univariant lines are 3-dimensionally curved lines but for simplicity are shown as straight lines. These lines and points do not lie in a plane. Only their relations to one another are shown in this diagram, which is not intended to depict their angular spatial relations. The lengths of the lines and the position of a temperature maximum on a line are arbitrary and without significance. Arrows indicate the direction of falling temperature. Abbreviations for crystalline solid phases along the lines and at the points: *LC* = leucite, *COR* = corundum, *MU* = mullite, *SP* = spinel, *CORD* = cordierite, *SAP* = sapphirine, *FEL* = potassium feldspar, *TR* = tridymite, *CR* = cristobalite, *FO* = forsterite, *PR* = protoenstatite, *EN* = enstatite. (After SCHAIRER.)

with H_2O and FeO. Furthermore the actual compositions themselves are useful as a basis for addition of other components, such as H_2O. Thus certain limited portions of the system K_2O–MgO–FeO–Al_2O_3–SiO_2–H_2O might be studied, and reveal the stability relations of a large group of minerals occurring in igneous and metamorphic rocks. The most important results on this series of joins is best given by a single "Schairer diagram" (Fig. 59). Inspection of this diagram shows that as a result of a number of quaternary peritectic points, crystallization in this portion of the system trends, particularly with crystal fractionation, toward two low-temperature eutectics, points *E* and *K*, which correspond essentially to potash granites, with very minor amounts of cordierite, and mullite or pyroxene (enstatite). This illustrates what will probably be found to be a general phenomenon in complex silicate systems; there will probably be far more peritectic (reaction) invariant points than eutectic points. This of course results in far greater effects for any crystal fractionation, as a liquid must stop at a eutectic, with or without fractionation, but with fractionation it will go right on past a reaction point where it should stop, at equilibrium. One other important fact, apparent from Fig. 59, is that certain planes in such a system act as barriers to liquids changing with crystallization, whether at equilibrium or with fractionation, and hence partition the diagram into regions, each with its own residual liquid goal.

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CONCLUSION

The major purpose of the silicate phase equilibrium research covered in this review was to aid in the understanding of igneous rocks, and in this respect it has been eminently successful. In addition, it has been of great help in the study of slags, refractories and cements. The systems described have immediate application to many problems in igneous petrology, and with the addition of volatiles under pressure, or pressure alone, they may be extended to cover rather closely the conditions of formation of most igneous and many metamorphic rocks in the crust of the earth. Obviously, the greater the difference in composition, or pressure, from the conditions under which the diagram was determined, the greater the possible errors in extrapolation, but the "dry" systems presented here still provide the necessary firm base on which experimental or theoretical extensions must be built.

As for the future, there are many important additional dry silicate melt systems that have not been determined. Some of the more important of these, such as the pyroxene quadrilateral, $MgO \cdot SiO_2$–$CaO \cdot MgO \cdot 2SiO_2$–$CaO \cdot FeO \cdot 2SiO_2$–$FeO \cdot SiO_2$, are currently under investigation, but others have not even been started. The procedure described by MUAN (1955, 1957) for controlling the oxygen pressure over melts, and hence the state of oxidation of variable valence elements in the melt, should be applied to a variety of complex systems to aid in understanding the great influence of oxidation state on differentiation trends in iron-rich magmas such as basalt, as well as to study the geochemistry of other variable-valence elements such as manganese, titanium, sulphur, etc. Much work is needed on the distribution of all trace elements between liquid and various crystallizing phases under various conditions of temperature and composition. Radioactive tracer techniques should be particularly useful here.

Much of the silicate phase research up to the present has been in the area between the liquidus and solidus; this is admittedly the most significant part for

igneous petrology, but when effects such as inversion or exsolution appear on cooling, studies of the subsolidus region are obviously needed, and may yield much information on the thermal history of the rock as well as on metamorphic processes. These subsolidus reactions are slow to equilibrate and hence experimentally difficult, but are gradually being unravelled by a variety of techniques including sintering, high temperature X-ray diffraction, and thermochemical measurements and calculations (see, for example, SAHAMA and TORGESON, 1949, and KRACEK and NEUVONEN, 1952).

One particularly important purpose of silicate research, in which considerable advances can be expected in the future, is to gain an understanding of the liquid phase. Knowledge of the liquid phase has lagged behind that of the solid, crystalline phase and there are many phenomena involving silicate glasses that are not fully understood at this time. A good example is the "acclimation" of a non-crystallizable glass of albite composition, formed at 1600°, by successive lower heat treatments, to permit ready crystallization at subliquidus temperatures (SCHAIRER, 1951, p. 282). The liquidus curves for substances may have a variety of shapes, depending on the thermal properties of the crystals and liquid and the effects of any interactions in the liquid causing deviation from ideality (see, for example, BOWEN and SCHAIRER, 1929a). The ionic species present in liquid silicate melts may be investigated by electrical methods, but the experimental techniques are difficult (EITEL, 1954b). KNAPP and FLOOD (1957) have calculated the activities in borosilicate melts to evaluate various structural models, and have extended their work to melts between $CaO \cdot SiO_2$ and SiO_2.

Viscosity, density and X-ray measurements on silicate melts have also provided considerable information about their nature. Most density determinations have been made on the quenched glasses at room temperature, from which partial molar volumes may be calculated (CALLOW, 1952); precision determinations of the density of glasses by the density gradient method (HORN, 1955) should aid these studies. A short but excellent review of the crystal chemical explanation of magmatic differentiation is given by OSBORN (1950), and further studies of this nature are in order. Investigations such as these provide a better understanding of the nature of the bonding in silicate melts and may actually permit prediction of phenomena such as immiscibility (LEVIN and BLOCK, 1957; BLOCK and LEVIN, 1957).

In general, however, it is safe to say that silicate systems must still be determined experimentally as this is usually less difficult than obtaining the experimental data needed to calculate them, particularly where the deviations from ideality are large. In this connexion a quotation from N. L. Bowen is apropos. In a presidential address in 1937 (BOWEN, 1938, p. 124) he wrote the following concerning the status of the calculation of silicate phase diagrams when he first joined the Geophysical Laboratory in 1912:

> "There were then enthusiastic thermodynamicians who wagered that within five years such advance would occur in thermodynamic theory and in the measurement of fundamental thermodynamic quantities for silicates that it would no longer be necessary to determine silicate equilibrium relations experimentally; instead they would be determined by a few simple calculations. Five times five years have passed since those sanguine days yet it is still necessary to determine silicate equilibrium diagrams by means of experiment."

Although considerable progress has been made in the twenty years since Bowen wrote this, it appears that silicate diagrams must still be determined experimentally.

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THE GEOCHEMISTRY OF THORIUM AND URANIUM[1]

By JOHN A. S. ADAMS, J. KENNETH OSMOND and JOHN J. W. ROGERS

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I. INTRODUCTION

EVER since natural radioactivity was first discovered in uranium ore by BECQUEREL (1896), uranium and then thorium have been of increasing geologic and geochemical interest. At first, much of this interest centred around the possibilities of absolute geologic dating according to the methods developed since the early years of this century. Nearly forty years of intense scientific interest and activity in absolute dating methods were completely dwarfed by the interest and activity generated by the military and industrial applications of uranium and thorium as nuclear energy sources. Recent review articles touching on the general geochemistry of thorium and uranium have emphasized the dating aspects (e.g. WILSON, RUSSELL and FARQUHAR, 1956) or the economic aspects (e.g. MCKELVEY, EVERHART, and GARRELS, 1955; U.S.G.S. Prof. Paper 300, 1956; and *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, Vol. 6, 1956). The primary purpose of this article is to summarize briefly the data and thought regarding the major geochemical cycles of thorium and uranium in the common rocks and minerals that make up over 99 per cent of the accessible earth, but which are not now of direct interest for geologic dating or economic development. However, it is almost needless to point out that there are many intimate and interesting relationships between the general geochemistry of thorium and uranium and the problems of geologic dating and economic development.

Another special aspect of the geochemistry of thorium and uranium that attracted early interest was the heat produced in the earth by the radioactive disintegration of thorium, uranium, and their daughters. Much of the early work of JOLY (1909) and others on the average thorium and uranium contents of rocks was done to estimate the heat produced by natural radioactivity. Many of Joly's pioneer determinations are gratifyingly close to modern estimates. After Joly, only a small amount of currently acceptable data on general abundances was produced until EVANS and GOODMAN (1941) published their survey and summary. These last authors also discussed the failings of the previously used analytical techniques. Since about 1947 the number of available uranium determinations on common rocks has increased many-fold. However, the lack of suitable analytical techniques has restricted greatly the number of available thorium determinations as the summaries in *Nuclear Geology* (Edited by H. FAUL, 1954) clearly indicated. The publication in the last year or two of a large amount of new data on the distribution of thorium and uranium, particularly in sedimentary rocks (BARANOV, RONOV, and KUNASHOVA, 1956; and ADAMS and WEAVER, 1958), permits a more detailed discussion at this time of the geochemical cycles of thorium and uranium. Doubtlessly the data that can be anticipated with confidence in the next few years will call for an early revision and extension of the present concepts.

The extensive literature on the geology, and particularly the economic geology of uranium has been given recently in several compilations and bibliographies (references cited above, and COOPER, 1953, 1954; CURTIS, 1957; and the *International Bibliography on Atomic Energy* and Supplements, 1951, 1952, 1953). Essentially the same situation prevails with the much less extensive literature on the geology and geochemistry of thorium (references cited above and *Gmelins Handbuch der anorganischen Chemie* **44**, 1955; BUCK, 1954; and DAVID, 1953). Other extensive reference lists are found in RANKAMA and SAHAMA (1950) and KOHMAN and SAITO (1954); and GRIMALDI (1956) lists over 100 papers covering the analytical chemistry of uranium and thorium. In consideration of the excellence of these bibliographies, only the more recent and major sources of bibliographies, together with the papers directly cited, are given in the list of references at the end of this article. In citing papers, many papers dealing with uranium alone have been omitted in favour of those which discuss both thorium and uranium geochemistry.

A strenuous effort has been made to consider all papers that appeared before the end of 1957 and as many as possible after that date. However, the delays in obtaining some journals and abstracts, as well as translations, have frustrated this intention to some unknown extent. In this regard, the Russian literature is particularly difficult to survey. DAVIDSON's (1957) recent review of Russian radiogeology is an excellent statement of the problem involved. The writers would consider it a favour to have any omission called to their attention. For purposes of uniformity, and because it is impossible to specify the oxidation state of uranium in many cases, all values for uranium and thorium are given as the metal in parts per million (p.p.m.; equivalent to grammes/metric ton) by weight.

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II. ABUNDANCES IN METEORITES, TEKTITES, AND THE COSMOS

The conclusions regarding the cosmic abundances of thorium and uranium are based upon: (1) determinations on extra-terrestrial material (meteorites) and possible extra-terrestrial material (tektites); (2) theoretical considerations involving nuclear stabilities, electronic configurations, and cosmological effects of heat due to radioactivity; (3) determinations on terrestrial rocks. Undisputed spectrographic evidence of the presence of thorium and uranium in the atmospheres of the sun, stars, nebulæ, or in interplanetary dust is lacking. Thus, the cosmic abundances of thorium and uranium must be quite low; however, it should be noted that spectrographic techniques are not particularly sensitive to thorium and uranium.

Meteorites

A considerable amount of ingenuity and effort has been devoted to the difficult problem of determining thorium and uranium in meteorites. Recent determinations by a variety of analytical techniques are cited in Table 1. The data in Table 1 indicate that older determinations were generally too high owing to analytical difficulties (see DAVIS, 1950, and other papers cited in Table 1). The data in Table 1 agree with older work in having thorium three or four times more abundant than uranium in many meteorites. Indeed, many workers (e.g., HURLEY, 1957) consider that a Th/U ratio of between 3 and 4 is sufficiently

Table 1. Thorium and Uranium Contents of Meteorites

Type	U (p.p.m.)	Th (p.p.m.)	Th/U	Reference and Method
Aerolites				
1 achondrite	0·01	—	—	DAVIS (1950); vacuum fusion and emanation determination
1 achondrite	0·048	—	—	*Ibid.*
1 chondrite	0·106	0·335	3·2	CHACKETT *et al.* (1950); emanation method
1 achondrite	0·010	—	—	PATTERSON *et al.* (1953); isotope dilution
1 chondrite	0·011	—	—	*Ibid.*
4 chondrite av.	0·024	0·080	3·5	HURLEY (1957); α counting and assuming Th/U is 3·5
1 achondrite	—	0·0055	—	BATE *et al.*, (1957); neutron activation
1 chondrite	—	0·043	—	*Ibid.*
1 chondrite	0·01	0·04	4·0	*Ibid.*
1 chondrite	0·01	0·047	4·7	*Ibid.*
1 chondrite	0·013	0·090	6·9	*Ibid.*
1 chondrite	0·011	0·045	4·1	*Ibid.*
1 achondrite	0·13	0·54	4·2	*Ibid.*
				uranium values from HAMAGUCHI, *et al.* (1957); neutron activation
4 aerolite av.	0·24	—	—	STARIK and SHATS (1956); neutron activation and luminescence method
Siderites				
Average of 6	0·007	0·04	6·0	ARROL *et al.* (1942); emanation method
Average of 7	0·0033	—	—	DAVIS (1950); vacuum fusion and emanation determination
Average of 15	0·006	0·025	—	DALTON *et al.* (1953); emanation method, α counting, and fluorimetric U
Average of 3	0·019	—	—	STARIK and SHATS (1956); neutron activation and fluorimetry
Results on 2	< 0·0005	—	—	REED and TURKEVICH (1955); neutron activation
Results on 2	< 0·006	< 0·02	—	DEUTSCH *et al.* (1956); nuclear emulsion

well established to be assumed as a constant. Thus, it is important in Table 1 and in other connexions cited below to distinguish between those data that represent experimentally determined Th/U ratios and those data that are calculated on the assumption that the Th/U ratio in meteorites is between 3 and 4. Undoubtedly there is some real variation in the thorium and uranium contents among meteorites and within single meteorites like certain of the chondrites. However, there are definite indications that some of the observed variation is only apparent and may be assigned to analytical errors. One must note that results on the same meteorites by different investigators have differed by a factor of 5 or 10 (see BATE *et al.*, 1957). Of the recent determinations, the uranium values of STARIK and SHATS (1956) are much higher for both aerolites and siderites.

In view of the uncertainty and paucity of the available data, it is difficult to estimate the average thorium and uranium contents of meteorites. The aerolites listed in Table 1 generally have a uranium concentration between 0·01 and 0·1 p.p.m.; the thorium concentration is generally two to five times that of uranium. Compared to the aerolites, the siderites have much lower uranium

concentrations (0·005 p.p.m. or less) with the thorium again being perhaps two to five times higher. Most cosmologists now feel that chondrites represent an average of all meteorite material (SUESS and UREY, 1956, and HURLEY, 1957). LEVIN, *et al.* (1956) in a recent Russian journal, report thorium and uranium averages in meteorites (thorium = 0·20 p.p.m., uranium = 0·05 p.p.m.) that are within the range of averages given here.

One may hope that if the recent research activity on meteorites continues, the thorium and uranium abundances in meteorites will become better known in a few years. However, the present situation is only slightly better than that reported by SUESS and UREY (1956) in their discussion of cosmic abundances.

Tektites

Obviously tektites are part of the cosmos, but there is some question as to whether they are terrestrial or extra-terrestrial material (see FRIEDMAN, *et al.*, 1958). Because tektites may be extra-terrestrial, the data on their thorium and uranium contents are listed in Table 2 and discussed in connexion with the meteoritic data. The early work of DUBEY (1933) established that tektites contained more thorium and uranium than any undisputed meteoritic material (see Tables 1 and 2). Dubey does not describe his analytical methods in any detail nor does he estimate his errors. However, the later work of ADAMS *et al.* (1953), and ADAMS (1956), together with that of Friedman (in FRIEDMAN, *et al.*, (1958) and TILTON (1958) indicates that Dubey's thorium values are essentially correct. Many of Dubey's thorium values are 25–50 per cent higher than the few most recent determinations.

The limitations of the data in Table 2 permit only a few tentative conclusions regarding the thorium and uranium geochemistry of tektites. The data indicate that: (1) in comparison with undisputed meteoritic material, the tektites have greater thorium and uranium contents and they probably have a much greater range in Th/U ratios; (2) in comparison with sedimentary rocks, the tektite data are quite comparable to sediments of shaly sand to shale composition (see section on sedimentary rocks below); (3) in comparison to igneous rocks, the thorium and uranium contents of tektites are in the andesite to dacite range, although there are not enough data to determine whether or not the range in Th/U ratios is comparable.

Theoretical Considerations

Limits on the cosmic abundance and distribution of thorium and uranium can be calculated by two independent methods. One method gives an upper limit for the modern concentrations of potassium, thorium, and uranium that a body of planetary size can have without having melted. UREY (1955) refined previous calculations of this type, using the latest and most accurate physical data on disintegration rates and energies. He calculated an upper limit of 276 p.p.m. potassium, 0·105 p.p.m. thorium, and 0·033 p.p.m. uranium for a body the size of the earth. The relative proportions of the three elements are those found in meteorites. The limits and arguments given by Urey regarding planetary heat balances indicate that bodies like the earth must have lower mean concentrations of thorium and uranium than many of the chondrites and achondrites listed in Table 1. On the other hand, the mean densities of planetary bodies indicate a bulk composition more like the chondrites and achondrites than the

Table 2. Thorium and Uranium Contents of Tektites

Sample	Uranium (p.p.m.)	Thorium (p.p.m.)	Th/U	Author and Method
Moldavite	3·0*	10·8	3·6*	DUBEY (1933), fusion-emanation
Moldavite	2·9*	16·0	5·5*	*Ibid.*
Moldavite	2·2*	16·0	7·3*	*Ibid.*
Moldavite	2·8*	18·6	6·6*	*Ibid.*
Billitonite	2·7*	9·6	3·6*	*Ibid.*
Australite	2·7*	5·0	1·9*	*Ibid.*
Australite	2·4*	18·4	7·7*	*Ibid.*
Darwin Glass	1·4*	11·3	8·1*	*Ibid.*
Darwin Glass	1·9	—	—	ADAMS (1956), α-counting-fluorometric U
Bediasite	1·2	4·7, 7·0†	3·9, 5·8†	ADAMS (unpublished), α-counting-fluorometric U
Bediasite	1·2	3·9	3·3	*Ibid.*
Bediasite	1·2	3·3	2·8	*Ibid.*
Bediasite	1·5	—	—	ADAMS (1956), fluorometric U
Indochinites, Composite A	1·6	—	—	*Ibid.*
Indochinites, Composite B	1·7	—	—	*Ibid.*
Moldavites Composite	1·8	—	—	*Ibid.*
Phillipinites Composite	1·6	—	—	*Ibid.*
Australites Composite	1·7	—	—	*Ibid.*
Australites Composite	1·7	—	—	*Ibid.*
Australites Composite	1·5	—	—	*Ibid.*
Australites Composite	1·5	—	—	*Ibid.*
Australite, S. Australia	1·74	9·19	5·3	TILTON (1958), isotope dilution

* Calculated from data in original paper.
† Thorium determined colorimetrically.

siderites, the latter having thorium and uranium concentrations well below the limits quoted. SUESS and UREY (1956) have discussed the difficulties of reconciling all the evidence. At present it appears that some of the cited values on chondrites and achondrites are either too high owing to analytical errors or that these meteorites have been enriched in thorium and uranium relative to the siderites, the planets, and mean cosmic material (see HURLEY, 1957).

Other theoretical limits on cosmic abundances can be estimated on the basis of observed periodicities between the abundance and the nuclear characteristics of the elements. The literature of forty years' effort in these directions has been reviewed by RANKAMA (1954) and SUESS and UREY (1956). A number of

empirical rules for all the elemental and isotopic abundances have been developed and related to nuclear binding energies. The following are some of the observations which are fully consistent with the rules that have been developed: (1) thorium is and always has been more abundant than uranium; (2) thorium and uranium, with even proton numbers, are much more stable and much more abundant than the odd proton number elements on either side of them in the actinide series; (3) uranium-238, with an even number of neutrons, is more stable and always has been more abundant than uranium-235, which has an odd number of neutrons. These and many other similar agreements between observations and the rules that have been established have led to attempts to construct smooth curves of abundance as a function of nuclear characteristics. On the basis of such smooth curves, SUESS and UREY (1956) have estimated the cosmic abundance of uranium to be between 0·0063 and 0·063 uranium atoms per million silicon atoms, which would indicate a cosmic concentration of 0·01 to 0·1 p.p.m. They estimate that thorium is 3 to 3·5 times more abundant than uranium. It should be noted that SUESS and UREY give these estimates in their text only and that thorium and uranium are the only elements omitted from their tabulation of cosmic abundances.

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Terrestrial Rocks

It is quite evident that terrestrial rocks are greatly enriched in thorium and uranium relative to the cosmos (see below). There is also substantial evidence from the determinations on igneous rocks (see Tables 4 and 7) and average terrestrial quartz (MURRAY and ADAMS, 1958) that in accessible terrestrial material the mean Th/U ratio is probably between 3 and 4. This evidence, together with that cited above, indicates that the Th/U ratio in the cosmos is between 3 and 4 at present, providing that it is also concluded either that the bulk of the earth's thorium and uranium is in the crust, or that there is no important shift in Th/U ratio as one moves from the core of the earth to the outer 40 km or so. This last conclusion appears reasonable because of the close chemical similarities between thorium and uranium when they are both in the tetravalent state to be expected under the reduced conditions hypothesized for the interior of the earth.

Thus, although the cosmic abundances of thorium and uranium can only be estimated to within one order of magnitude, the Th/U ratio in the cosmos at present is almost certainly between 3 and 4. It is interesting to note that terrestrial radiogenic lead isotopic ratios also require a Th/U ratio of about 3 or 4 (see page 306 and RANKAMA, 1954).

III. THE DISTRIBUTION OF THORIUM AND URANIUM AMONG THE CORE, MANTLE, AND CRUST OF THE EARTH

Ever since STRUTT (1906) and others recognized the importance of radioactivity as a source of heat inside the earth, there have been attempts to relate the thermal characteristics and history of the earth with the distribution and abundance of the major natural sources of radioactivity, namely, thorium, uranium and potassium. The numerous recent reviews of these attempts and related topics (e.g., BIRCH, 1954; JACOBS, 1956; and VERHOOGEN, 1956) emphasize the continuing interest and numerous difficulties. To develop an adequate thermal model of

the earth, it is clear that a number of factors are still to be reconciled. On one hand, the determinations of the abundance of thorium, uranium and potassium in the accessible portion of the crust set a limit for the production of heat from radioactive sources in that portion of the crust. On the other hand, the determinations of heat flow to the surface set a maximum limit on the amount of heat produced and transferred from all sources. Quantitative calculations involving these limits vary with the assumptions regarding such unknowns as the importance of convection currents in the mantle, primary heat, and heat conductivities under high pressures of the magnitude found in the mantle and below. Despite the quantitative uncertainties, it is evident that the concentration of thorium and uranium must fall off rapidly with depth, else the earth would be molten today. In fact, a large portion—perhaps three-quarters or more—of the earth's thorium and uranium is probably in the crust. Such qualitative discussions have been useful in many ways, e.g., the recent work of HURLEY (1957) on chondritic meteorites to see if their true thorium and uranium concentrations were low enough for the mantle to be of chondritic composition.

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It is difficult to interpret at this time the results of heat flow measurements with respect to the distribution of thorium and uranium in the outer mantle and in the crust. One might expect that continental heat flow, due to the higher content of the radioelements in a granitic or intermediate crust, ought to be at least twice the heat flow of ocean basins underlain by a relatively thin basalt layer (BIRCH, 1954). However, measurements by REVELLE and MAXWELL (1952), and BULLARD (1954) on the ocean bottom, and by BIRCH (1956) on a coral island, indicate that oceanic heat flow is about the same as that of the continents.

As regards the thermal history of the earth, there can be little doubt that the rate of heat production from thorium and uranium has markedly declined as these elements have decayed. Table 3 (after BIRCH, 1954) shows the greater

Table 3. Change in Rate of Heat Production by Natural Radioactivities in Geologic Time

(after BIRCH, 1954)*

Time (10^9 years)	1	2	3	4	5
Isotope					
Uranium-238	1·08	1·17	1·27	1·38	1·51
Uranium-235	1·70	3·11	6·09	12·60	27·20
Uranium (common)†	1·11	1·25	1·47	1·85	2·57
Thorium-232	1·03	1·05	1·08	1·11	1·14
Potassium-40	1·33	1·82	2·55	3·65	5·33

* The present rate of heat production = 1·00 in each case.
† With modern uranium-238/uranium-235 = 139.

heat production in the past, setting the present heat production of each element at 1·00. At present, taking a Th/U ratio of about 3·5, the half-lives and disintegration energies are such that the thorium and uranium series each produce heat at about the same rate and together they produce heat at a rate about six

times greater than that of potassium in common granites (see BIRCH, 1954). In discussing the importance of radioactivity in the very early thermal history of the earth, it must be noted that short lived, and now extinct, radioactivities may have made a contribution (KOHMAN and SAITO, 1954).

Aside from the thermal considerations discussed above, there are three other lines of evidence regarding the distribution of thorium and uranium among the crust, mantle, and core. The first line of evidence is the classical geochemical approach of GOLDSCHMIDT (edited by MUIR, 1954) by which thorium and uranium are both classified as lithophile (or oxyphile in these two cases) on the basis of their mineralogy and general chemistry, including valence states, ionic radii, and oxidation potentials (see next section). The strong oxyphile or lithophile characters of thorium and uranium would require that they be concentrated in the crust or oxysphere relative to the mantle or core. This interpretation agrees fully, of course, with that based upon the thermal considerations discussed above.

The second supporting line of evidence is based on the assumption that the earth's crust and mantle were derived originally from chondrite-like material. If this is true, then the mantle must be greatly depleted in its thorium and uranium in order to compensate for the measured amounts in crustal materials. PATTERSON *et al.* (1955) hypothesize that 90 per cent of the earth's uranium would be concentrated in a crust composed of 5 km of granite and 25 km of basalt.

A third convergent line of evidence is based on interpretations of isotopic analyses of common leads. A remarkable feature of such leads is the world-wide nearly uniform increase with time of the radiogenic components, lead-206, lead-207, lead-208, which are derived from radioactive decay of uranium and thorium (for general discussion, see FAUL, 1954). Calculations show that the elemental ratios required to produce these radiogenic increases in the source of common leads are consistent with the measured thorium, uranium, and lead concentrations in the earth's crust, especially the basic and intermediate portions of the crust. Even the "anomalous" leads, which are common leads characterized by higher than normal amounts of radiogenic isotopes, may be explained by assuming a considerable growth period in a source with elemental ratios similar to those found in granites and shales:

	U^{238}/Pb^{204}	Th^{232}/U^{238}
Normal leads reservoir	8–10	3·5
Basalts	7	3–6
Anomalous leads reservoir	15–50	3–6
Granites and shales	15–25	3–6

Certain small secular changes in the elemental ratios of the source of common leads have been observed, such changes being unaccountable by simple decay of uranium and thorium, and it has been suggested that leads of lower radiogenic composition are possibly being added to the crust from the mantle relative to thorium and uranium (MARSHALL, 1957; and RUSSELL, 1956).

IV. DISTRIBUTION OF THORIUM AND URANIUM IN THE EARTH'S CRUST

The Chemistry, Geochemistry, and Mineralogy of Thorium and Uranium

Many of the researches to be cited here have been directly connected with and supported by various governmental programmes directed primarily toward the development of raw material supplies for nuclear weapons and power. In addition to such direct geological and geochemical studies, the many extensive and fundamental studies of the chemistry and toxicity of thorium and uranium are great resources where attempting to understand the distribution of thorium and uranium in the accessible crust. Fortunately many of these studies are now generally available, particularly in such recent compilations as the *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* (1955), *U.S. Geological Survey Prof. Paper* 300 (1956), the *National Nuclear Energy Series* (from 1949 on), and the eighth edition, Thorium Volume of *Gmelins Handbuch der Anorganische Chemie* (1954). Annual reviews of the analytical chemistry of thorium and uranium have been presented frequently in *Analytical Chemistry* (from 1949 on). The several special sources of abstracts and bibliographies of pertinence have been given above. To facilitate later discussions, some of the most salient properties of thorium and uranium are summarized briefly in the following sections.

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The many strong chemical and geochemical similarities between thorium and uranium can be related fundamentally to similarities in their outer electronic configurations that led to their classification as actinides (see SEABORG and KATZ, 1954). Although there are some objections to the term actinides (e.g. ZACHARIASEN in SEABORG and KATZ, 1954), it will be used here because of its wide acceptance and usefulness. Indeed, this brief review could be considered a review of the geochemistry of the actinides, because thorium-232, uranium-235, and uranium-238 are the only actinide nuclides that have persisted through the history of the earth; the other actinide nuclides (see SEABORG and KATZ, 1954) are either not found in nature or are found only in close association with thorium and uranium, where they have an extremely low abundance and a very transitory existence in geologic time.

The electronic configuration of the actinides has been reviewed by SEABORG (1954), DAWSON and HALL (1956), and FRIED and ZACHARIASEN (1956). It appears that in some respects the electron back-filling of the 5*f* shell in the "5*f*" (actinide) series is more complicated than in the corresponding "4*f*" (lanthanide) series, due to the proximity of energy levels of the 6*d* and 5*f* shells. However, in cases where thorium and uranium are both in the tetravalent state, they have identical outermost electron configurations. Furthermore, the ionic radius of tetravalent uranium is only a few per cent smaller than that of tetravalent thorium. Unfortunately, there is some confusion in the literature regarding the exact values for these radii. Aside from experimental variations, this confusion arises from the use of different units (*kX* and Ångströms), the use of different values for the radius of the oxygen ion, and the failure in some cases to specify whether ionic, covalent, or metallic bonding is meant. ZACHARIASEN (1954) has reviewed the crystal chemistry and the values for the ionic radii of all of the actinides. The essential points are that there is no difference in the outermost electron shell configuration, or co-ordination number (eight) with

respect to oxygen, and very little difference in size between tetravalent thorium and tetravalent uranium.

Tetravalent cerium and the somewhat smaller tetravalent zirconium and hafnium ions all have marked chemical similarities to tetravalent ions of thorium and uranium. The chemical similarities among the tetravalent ions of these five elements can be related to their similar ionic sizes, equal co-ordination number (eight) with respect to oxygen, and the completeness of their outermost electron shell. FRONDEL (1956) has illustrated the fundamental importance of these considerations in understanding the many close geochemical and mineralogical similarities between these five elements. Thorium, hafnium, and zirconium in particular, because they occur only as tetravalent ions in nature, tend strongly to remain together. Their separation in nature or in the laboratory is difficult. Among the many chemical examples that might be cited to illustrate the close chemical similarities, mention might be made of the great effort that was required to develop methods for the preparation of hafnium-free, reactor grade zirconium metal; additional examples are also provided by the many difficulties encountered in developing a chemical method for the microdetermination of thorium in ordinary rocks where a Zr/Th ratio of 10 to 20 is the general case. Indeed, the interference of zirconium with the micro-determination of thorium is one of the main reasons why there are so few data on the thorium content of rocks. By contrast, there are many more data on the uranium content of common rocks, and this situation arises primarily from some unique chemical properties of uranium that make its separation and determination much easier than is the case with thorium.

The unique chemical properties of uranium relative to thorium can be related in a fundamental way to the two extra electrons that uranium has in the inner, unfilled (5*f*) electron shell. These two electrons can also be valence electrons in addition to the four outermost electrons in the uranium atom. Thus uranium, unlike thorium, has the possibility of either a pentavalent or a hexavalent state. The pentavalent state of uranium, like the trivalent state of thorium or uranium, has only a transitory existence in the laboratory and is not to be expected under geologic conditions (see SEABORG and KATZ, 1954). The hexavalent state of uranium, on the other hand, is very stable and is found in over two-thirds of the hundred odd minerals in which uranium is a major (greater than 1 per cent) component (see FRONDEL and FLEISCHER, 1952). In systems where oxygen is a major component, which include minerals, most common salts, and solutions, hexavalent uranium is found to be closely associated with two oxygen ions, forming the very stable, divalent uranyl ion (UO_2^{++}) (see SEABORG and KATZ, 1954; and CHRIST *et al.*, 1955). Unlike the essentially spheroidal tetravalent thorium and uranium, the divalent uranyl group is a "dumb-bell shaped" group with the centres of the two oxygen ions and the hexavalent uranium ion lying on a line with the smaller uranium in the centre. The uranyl ion is an entirely different chemical species from tetravalent uranium; one of the most geochemically important differences is the generally much greater solubility of uranyl compounds relative to those of tetravalent uranium. Although the majority of uranium minerals contain hexavalent uranium, it must be noted that most of these minerals are found near the surface in the zone of weathering and oxidation. Thus, it is possible that much of the uranium in the crust, which is contained largely in igneous rocks below the zone of oxidation, is in the

tetravalent state. In any case, it is of the utmost importance in understanding the geochemistry of thorium and uranium to delineate as far as possible the chemical conditions under which uranium is hexavalent and those under which it is tetravalent.

The chemical conditions under which tetravalent uranium is oxidized to hexavalent uranium (usually in the form of uranyl ion) are characterized in terms of the oxidation potential (see LATIMER, 1952). In a closed chemical system the oxidation potential may vary with the composition, temperature, and pressure of that system. As regards composition, the geochemical importance of pH or hydrogen ion concentration is well known in general (MASON, 1952); and GARRELS (1955) in particular has shown how pH and oxidation potential computed as *Eh* may be used to indicate the stability fields of uranium ore minerals. The utility of such *Eh*–pH diagrams may be limited to geological situations where there are only a few major components, of which uranium is one. Such situations are rare, though of great economic significance. In the common geologic situation, where uranium is a trace element measured in a few parts per million, the oxidation relations involving uranium may be greatly complicated by the fact that there are many components in the system that are more abundant than uranium. In general, however, tetravalent uranium is oxidized to the hexavalent state about as readily as ferrous ion is oxidized to ferric; also, ferrous ion can be expected to reduce uranyl in many situations, and this may explain the frequent hematitic haloes and occurrences around pitchblende veins (MCKELVEY *et al.*, 1955). However, there are geochemically significant systems where the relative oxidation potentials of ferrous ion and tetravalent uranium may be reversed. One such system is the phosphate-rich system investigated in detail by BAES (1956), ALTSCHULER *et al.* (1956), and CHENTSOV (1957). BAES identified a phosphate–tetravalent uranium complex that was stable enough to reverse the usual oxidation potential relationship with ferrous ion. The probable importance of such phosphate-complex mechanisms in the fixation of uranium in phosphate rocks will be discussed in the section on sedimentary rocks.

Aside from the phosphate complex just discussed above, there are many other known complexes involving thorium and uranium (KATZ and RABINOWITCH, 1951; SEABORG and KATZ, 1954). Most of these are geochemically insignificant organic complexes, but several, like the uranyl-carbonate complexes, are of particular geochemical significance (MCKELVEY, *et al.*, 1955). This tendency of thorium and uranium to form complexes with different anions, together with such factors as hydration–dehydration relationships between thorium and uranium hydroxides and the ability of both elements to form hydroxy double salts, makes difficult the important tasks of determining the effect of pH on solubility and oxidation potential relationships. Solubility relationships in dilute solutions are given by MILKEY (1954), and chemical properties of uranium oxides are discussed by GARRELS (1955).

As many modern versions of the periodic chart emphasize, the actinide series of elements is analogous to the lanthanide series in the manner in which electrons are added to the 5*f* electron shell as one moves to higher proton numbers in the series. The lanthanides are very similar chemically wherever they have their usual valence of three; only lanthanides with other possible valences, e.g. cerium, are strongly fractionated from the main group. In principle, both the

lanthanides and the actinides can be used as oxygen indicators, because their fractionation depends largely upon their state of oxidation. ADAMS and PLILER (1956) used this approach in attempting to determine whether the distribution of uranium and thorium in pre-Cambrian sedimentary rocks gave any indication of non-oxidizing pre-Cambrian atmosphere. ROBINSON *et al.* (1957) have made some studies on the distribution of lanthanides in soils as related to oxidation during weathering.

Only the most basic aspects of the mineralogy of thorium and uranium need be presented here, because there are recent and comprehensive reviews of the crystal chemistry of the actinides (ZACHARIASEN, 1954) and of the mineralogy of thorium as related to the mineralogy of uranium, cerium, zirconium and hafnium (FRONDEL, 1956). The ionic radii, high valences and electronegativities of thorium, uranium, cerium, zirconium, and hafnium make them a unique and cohesive group that, by virtue of these properties, cannot form significant isomorphic series involving major rock-forming minerals. Instead these five elements tend to be segregated into very minor accessory mineral phases that are dominated by the more abundant zirconium and cerium. Thus, zircon ($ZrSiO_4$), a ubiquitous but minor (x/10,000) part of granite and other common rocks, has been found to contain up to a few per cent of the less abundant thorium and uranium. This thorium and uranium is either present in simple isomorphic substitution for tetravalent zirconium or as optically continuous inclusions of the isomorphic thorite ($ThSiO_4$) (BUTTLAR and HOUTERMANS, 1951). Although zirconium, hafnium, thorium and uranium have the same co-ordination number of eight with respect to oxygen, zirconium and hafnium have ionic radii about 15 per cent smaller than thorium and uranium. This difference in ionic radii, as well as the lower abundance and availability of thorium and uranium, may limit the amount of thorium and uranium substitution for zirconium in zircon. In addition to tetragonal nesosilicates (orthosilicates) of the zircon type, a series of tetragonal nesosilicates of the thorogummite ($Th(SiO_4)_{1-x}(OH)_{4x}$) type is known; tetravalent uranium, cerium, zirconium, or hafnium may substitute isomorphously in the thorium position and the recently described uranium-rich member of this series, coffinite (STIEFF, *et al.*, 1955), has been found to be an important ore mineral. The only other silicates where thorium and uranium may be in isomorphic substitution in important amounts, are allanite (essentially $(Ca, Ce, Th)_2 (Al, Fe, Mg)_3Si_3O_{12}(OH)$) and sphene ($CaTiSiO_5$). In these two silicates, as in apatite ($Ca_5(Cl, OH, F)(PO_4,)_3$) the tetravalent thorium and uranium may be isomorphously substituting in the calcium position.

The cerium-rich monazite ($(Ce, Y, La, Th)(PO_4)$) rivals zircon in common rocks as a ubiquitous and important carrier of thorium. To a much lesser extent uranium is also found in monazite, apparently also in isomorphic substitution (see FRONDEL, 1956). The situation is reversed in the related, but less important xenotime (YPO_4), where uranium is generally more abundant than thorium. With the addition of uraninite (UO_2 ideally) and the partially isomorphous thorianite ($(Th, U)O_2$), mention has been made of those minerals found in common rocks that are believed to contain thorium and uranium as essential components in regular crystal structural positions.

The mineralogy of uranium in pegmatites (PAGE, 1950) and economic deposits has been intensely investigated, especially in the last few years, and, as a result,

a large number of these minerals have been described (FRONDEL, 1956). In particular, many uranyl-containing vanadates, phosphates, arsenates, sulphates, carbonates, etc. have been found in the oxidized zone of uranium occurrences. Because of the fine-grained nature of these oxidized deposits and the complex mineralogy resulting from the high solubility of the uranyl ion, it is often difficult to designate precisely the minerals present. In addition to such uncertainties in economic deposits, there is even a larger fraction of the crust's uranium and thorium contained in common rocks that cannot be localized as regular mineral components. The thorium in common shales and the uranium in certain black shales are examples of situations where these elements are so dispersed or their minerals so fine grained that they have not been assigned to identifiable minerals. The concentration of thorium and uranium in common rocks seldom exceeds 0·1 μmole/g of rock and even in well crystallized, coarse-grained rocks, much of the thorium and uranium may be occluded, adsorbed on crystal imperfections, or fixed in other dispersed sites before they are concentrated enough to enter into the stable mineral species described above. Quartz in granites is a case in point, because autoradiographs of granites (PICCIOTTO, 1950; and others cited on page 315) indicate that thorium and uranium occur in very small mineral or liquid inclusions in the quartz, and the analysis of quartz in beach sands (MURRAY and ADAMS, 1958) indicates that about 5 per cent of the thorium and uranium in granites can be expected to be so fixed in the quartz.

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Thorium and Uranium in Igneous Rocks

The following discussion of the distribution of thorium and uranium in igneous rocks is subdivided into three parts: first the average content in various igneous rock types; second, a discussion of the occurrence and variation of thorium and uranium within each rock type; and third, a summary of the possible behaviour of thorium and uranium during magmatic differentiation.

Average abundances. The average abundances of thorium and uranium in various igneous rock types are shown in Table 4. For the purposes of averaging, the rocks are divided into the following groups: (1) silicic intrusive (quartz-bearing rocks ranging from granite to tonalite plus syenite and monzonite); (2) silicic extrusive rocks (same compositional range as silicic intrusive); (3) basic intrusive (gabbro and diorite); (4) basic extrusive (basalt and andesite); (5) ultrabasic; (6) alkaline (any feldspathoid rock); and (7) silicic pegmatite. For the outer few kilometers or so of the earth's continental crust, where granitic rocks predominate, the average thorium and uranium contents appear to be 10–15 p.p.m. and 3–4 p.p.m. respectively with an average Th/U ratio of 3 to 4 (see compilations by PLILER, 1956; and WHITFIELD, 1958). These figures, which represent several thousand granitic rocks, are based mainly on the analysis of aggregate samples by a few workers (e.g. SENFTLE and KEEVIL, 1947). At deeper levels in the crust, where more and more basic rocks predominate, the thorium and uranium concentrations decline from the figures given.

Table 4 shows that in general the thorium and uranium contents of igneous rocks increase with increasing acidity or silica content. Thus, the average thorium and uranium contents of basic intrusive rocks are only about one-quarter of those given above for granites. Ultrabasic rocks are exceptionally low in both elements, and their determination in these rocks is particularly difficult (see DAVIS (1950) and the section on meteorites). That the amounts of

Table 4. Thorium and Uranium in Igneous Rocks

Rock	Thorium (in p.p.m.)	Uranium (in p.p.m.)	Th/U
Silicic intrusive	1–25	1–6	2–6
Silicic extrusive	9–25	2–7	4–7
Basic intrusive	0·5–5	0·3–2	3–4
Basic extrusive	0·5–10	0·2–4	3–7
Ultrabasic	low	0·001–0·03	
Alkaline		0·1–30	variable
Silicic pegmatite	1–2	1–4	0·4–1·5

Notes for Table 4 on thorium and uranium in igneous rocks:

The ranges in which most reported thorium and uranium analyses and Th/U ratios fall are shown in Table 4; rocks with compositions outside these ranges are uncommon, though by no means non-existent. EVANS and GOODMAN (1941) and KEEVIL (1944) describe both the thorium and uranium contents of a wide variety of rocks. Abundances of thorium and uranium are given by: KEEVIL (1938), for granitic and basaltic rocks; by SENFTLE and KEEVIL (1947), for granitic and intermediate rocks; by HURLEY (1956), for several rock types; and by WHITFIELD (1958) for granitic rocks. Uranium analyses are reported by: COATS (1956), for silicic extrusive rocks; by DAVIS and HESS (1949), for ultrabasic rocks; by HAMAGUCHI *et al.* (1957), for a basalt and a dunite; by ADAMS (1954b, 1955) for obsidian and for other volcanic rocks; by GOTTFRIED and LARSEN, Jr. (1954), for granitic rocks; by LARSEN, Jr. (1954), for a variety of rocks; by LARSEN, Jr. *et al.* (1956), for a number of rocks; by LARSEN, Jr. and PHAIR (1954), for several rocks; and by PHAIR (1955, 1956), for silicic intrusive rocks.

thorium and uranium in igneous rocks, however, are not solely related to silica content is shown by the high concentrations of both elements in the generally subsilicic alkaline rocks.

The variation in thorium and uranium abundances within rock types and even within individual plutons is commonly larger than the differences among the averages for the various igneous rock types given in Table 4. LARSEN, Jr. *et al.* (1956) and NEUERBURG (1956) have summarized the rather extensive data on the variation found in the uranium content of igneous rocks. The data on thorium are by no means as comprehensive, largely due to the fact that many of the analyses were made on aggregates or isolated individual samples, because of the analytical difficulties involved. The wide range in the Th/U ratios of important thorium and uranium carriers (e.g. zircon, monazite and xenotime (see Table 5)) make it impossible to assume that thorium will necessarily show a sympathetic or parallel variation with the known variation of uranium. The following measurements on two samples of the Pike's Peak granite may be more representative of the variations that may be expected (WHITFIELD, 1958):

	Th (p.p.m.)	U (p.p.m.)	Th/U
Sample 1	35·4	4·65	7·6
Sample 2	22·2	0·89	24·9

Thus, the distribution of thorium and uranium in igneous rocks is not solely controlled by bulk composition; the abundances of these two elements must

also be affected by such factors as variation in the thorium and uranium concentration of the original magmas and the consequent magmatic crystallization history.

Silicic intrusive rocks. The term "silicic intrusive rocks" is here taken to mean all quartz-bearing rocks (granites to tonalites) plus syenites and monzonites. The abundances of thorium and uranium in most of these rocks are 10–15 p.p.m. and 3–4 p.p.m. respectively. The average Th/U ratio is 3–4. Values much outside the above limits may represent "unusual" rocks.

Many studies have shown that thorium and uranium in intrusive rocks are concentrated in accessory minerals, either as separate grains or as inclusions in the major minerals (KEEVIL *et al.*, 1944; PICCIOTTO, 1950; COPPENS, 1951; HEE *et al.*, 1954; BROWN and SILVER, 1956; MERLIN *et al.* 1957). Both autoradiographic examination (see BOWIE, Editor H. FAUL, 1954) and analysis of mineral separates give variable data on the radioactivity of minerals in different rocks, but apparently much of the thorium and uranium is concentrated in normal accessory minerals such as zircon, apatite, and sphene. In some rocks allanite appears to be one of the major radioactive minerals (BILLINGS and KEEVIL, 1946; BROWN and SILVER, 1956); and the closely related epidote is also unusually radioactive in some rocks (KEEVIL *et al.*, 1944). Monazite and xenotime, where detected in the common rocks, are also important sources of radioactivity (HUTTON, 1947) and are usually more active than associated zircon. In a few ordinary rocks rare grains of uraninite (DEUTSCH and PICCIOTTO, 1956; and HAMILTON, 1958) and possibly torbernite (MERLIN *et al.*, 1957) carry an important fraction of the radioactivity in the rock.

Mineral separates from intrusive igneous rocks have been studied by a number of authors, and in Table 5 are given the ranges in which most of the reported thorium and uranium contents of both major and accessory minerals fall. The range of concentrations found in most minerals is broad, a fact which demonstrates the extreme variability of the occurrence of both thorium and uranium in intrusive igneous rocks. Even within individual plutons, the radioactivity of many minerals is variable, and individual zircon crystals have been found in which the uranium concentration varies greatly between zones (LARSEN, Jr. *et al.*, 1953). The radioactivity of zircons in a single pluton has been found to vary in general with the acidity or silica content, but there are wide variations within one rock type (LARSEN, Jr. *et al.*, 1956). Despite this variability, the average abundances shown in Table 5 demonstrate several fundamental conclusions in addition to the obvious fact that the accessory minerals are far richer in thorium and uranium than the major rock-forming minerals:

(1) The common accessory minerals such as zircon, apatite, and sphene generally contain less thorium and uranium than less abundant accessory minerals such as allanite, monazite and xenotime. The importance of these rare minerals is also shown by the ability of monazite and xenotime, but not zircon, to produce pleochroic haloes in the biotites studied by HUTTON (1947), and by the tendency of total radioactivity to be related to the allanite content of a suite of granitic rocks (BILLINGS and KEEVIL, 1946). Zircon is undoubtedly an important source of radioactivity in some rocks, but is probably only rarely the major source.

(2) In most accessory minerals the Th/U ratio is greatly different from the crustal and cosmic ratio of about 3·5. Monazite, for example, commonly

Table 5. Thorium and Uranium in Minerals of Igneous Rocks

Mineral	Thorium (in p.p.m.)	Uranium (in p.p.m.)	Th/U
Accessory			
Allanite	500–5000	30–700	5–10 (accessory)
	1000–20,000	?–100	high (pegmatite)
Apatite	20–150	5–150	1 (accessory)
	50–250 (?)	10–50 (?)	10–25 (coarse aggregate)
Epidote	50–500	20–50	2–6
Ilmenite		1–50	
Magnetite	0·3–20	1–30	variable
Monazite	25,000–200,000	500–3000	25–50
Sphene	100–600	100–700	1–2
Xenotime	low	500–35,000	low (0·01?)
Zircon	100–2500	300–3000	0·2–1 (accessory)
	50–4000	100–6000	1 (pegmatite)
Major			
Biotite	0·5–50	1–40	0·5–3·0
Hornblende	5–50	1–30	2–4
Potassium feldspar	3–7	0·2–3·0	2–6
Muscovite		2–8	
Olivine	low	0·01	
Plagioclase	0·5–3·0	0·2–5·0	1–5
Pyroxene	2–25	0·01–40	4–5
Quartz	0·5–6·0	0·1–5·0	2–5
	(2·0)*	(0·7)*	(3)*

* Based on quartz in orthoquartzitic beach sands (MURRAY and ADAMS, 1958).

Notes for Table 5 on thorium and uranium in minerals of igneous rocks:

The ranges in which most reported thorium and uranium analyses and Th/U ratios fall are shown in Table 5; only a few, possibly aberrant, minerals have values outside these ranges. For many accessory minerals, analyses of relatively coarse-grained material (e.g. from pegmatites) are more common than analyses of mineral separates from ordinary rocks. Also, more uranium analyses are available than thorium analyses, and consequently the range of normal uranium values is larger than the range of thorium values; thus, for example, higher uranium contents than thorium contents have been reported for pyroxenes, though in pyroxenes in which both thorium and uranium have been determined, the Th/U ratio is 4–5.

The thorium and uranium contents of a large number of minerals are given by KEEVIL (1944). HURLEY and FAIRBAIRN (1957) report the abundances and distribution of uranium and thorium in zircon, sphene, apatite, epidote, and monazite in a number of samples from granitic rocks and some other rock types. HURLEY and FAIRBAIRN (1955) also discuss the Th/U ratios of zircon, sphene, and apatite. TILTON, *et al.* (1954) report thorium and uranium contents of several minerals in a granite. The uranium contents of a number of minerals from various igneous rocks are reported by LARSEN Jr. (1954), GOTTFRIED and LARSEN, Jr. (1954), LARSEN, Jr., *et al.* (1956), LARSEN and PHAIR (1954), and PHAIR (1955). Thorium and uranium contents of different minerals are reported by: HUTTON (1951), for allanite; PHAIR (1955), for allanite; SMITH *et al.* (1957), for allanite; ADAMS and WEAVER (1958), for apatite; TILTON and NICOLAYSEN (1957), for monazite; and WEBBER *et al.* (1956), for zircon. The uranium content of apatite is reported by PHAIR (1956), and the thorium content of monazite and allanite is reported by MURATA, *et al.* (1957). MURRAY and ADAMS (1958) give the thorium and uranium contents of quartz in sandstones.

contains a great excess of thorium over uranium, and xenotime carries more uranium than thorium. This variation among the later-forming accessory minerals (monazite and xenotime) might be explainable by late-stage oxidation in the magma, but the absence of the normal Th/U ratio in relatively early-forming accessory minerals like apatite and zircon may simply be caused by selective crystallization of one element over another in these minerals. If much of the available uranium in the magma is originally present as uranyl ions, the different Th/U ratios in these early-forming minerals may result from their different abilities to attach and hold tetravalent uranium. For a discussion of the partition of thorium and uranium among various accessory minerals see HURLEY and FAIRBAIRN (1957). It is also possible that the wide spread in Th/U ratios reflects the effectiveness of stable complexes (e.g., tetravalent uranium phosphate (see BAES, 1956) in lowering the concentration of thorium and uranium that is available for inclusion in crystallizing phases at any given magmatic stage.

Complexes involving the uranyl ion might favour the formation of uranyl ion even where the total oxidizing capacity of the system has not changed. In general, the formation and stability of such complexes would be favoured by the high valences of thorium and uranium, by the fact that their concentration is many times lower than that of complexing anions such as phosphate and carbonate, and by lower temperature.

Though accessory minerals apparently contain much of the thorium and uranium in silicic intrusive rocks, some of the thorium and uranium is contained in major constituents such as quartz and the feldspars. The importance of these major minerals varies from rock to rock and is intimately related to the very central question of the average grain size of those accessory minerals where thorium and uranium may occur in isomorphic substitution. Familiarity with such thorium- and uranium-containing accessories as zircon, apatite, and monazite in placer beach sands, in heavy mineral suites of sandstones, and in the large grains detected in the usual petrographic examination of intrusive igneous rocks, may have lead to the doubtful conclusion that in intrusive silicic rocks these accessories are predominately of sand size and may be expected to concentrate in detrital near-shore sediments (KOCZY, 1949; and FRONDEL, 1956). On the contrary, the almost submicroscopic size of the centres of pleochroic haloes (see HUTTON, 1947, and others) as well as the submicroscopic size of many of the centres of radioactivity detected in quartz and other common minerals by autoradiography (see PICCIOTTO and others cited above) indicate that a substantial weight of the accessory minerals in question may be of sub-silt and clay size. The rather uniform content of common shales (see page 323) could be the result of these accessory and resistate minerals being of largely sub-silt size. MURRAY and ADAMS (1958) have shown that in common ortho-quartzitic sandstones the small amount of thorium and uranium present is contained in the quartz, with the separable zircon, etc. making an inconsequential contribution. They have also discussed the difficult problem of determining how much of the crust's thorium and uranium is contained in accessory, resistate minerals of sand size. The size distribution of these accessory minerals can be expected to vary widely, depending upon their thermal and crystallization history, including nucleation effects. This size variation in turn might affect the probability of the accessory minerals in question being included in common

minerals like quartz and feldspar. Thus, some of the wide variation in thorium and uranium contents in common minerals and individual plutons (see Table 5) may be due to variations in the grain size of the accessory minerals. However, with isomorphic substitution possibilities largely ruled out, there are several other mechanisms by which thorium and uranium may be fixed in major rock-forming minerals. Discussions of these possible and largely metastable mechanisms are given by NEUERBERG (1956), TAUSON (1956), TAUSON *et al.* (1956), and HAMILTON (1958). Briefly, the thorium and uranium contents of quartz, feldspar, and ferromagnesian minerals may also be attributed to one or more of the following: (1) entrapment in lattice imperfections; (2) entrapment in liquid inclusions; (3) deposition along fractures; (4) adsorption on crystal surfaces. Autoradiographic studies (PICCIOTTO, 1950; BROWN and SILVER (1956)) have also shown that in some rocks there is a concentration of thorium and uranium along grain boundaries as a kind of "paint". Leaching studies (HURLEY, 1950; BROWN, *et al.* 1953; BROWN and SILVER, 1956) have confirmed that these two elements and their daughters are readily leached out of many intrusive silicic rocks. Very fine-grained accessory minerals and secondary minerals such as allanite may contribute to this interstitial material, or it may be that the thorium and uranium are simply trapped between the major mineral grains as adsorbed ions.

Despite the erratic distribution of thorium and uranium within many suites of igneous rocks, several studies have shown that there is a general tendency for the radioactivity of a rock to increase with increasing silica content (BILLINGS and KEEVIL, 1946; LARSEN, Jr. and PHAIR, 1954; and LARSEN Jr. *et al.*, 1956). In some cases, however, alkaline end-members of igneous sequences are particularly enriched in thorium and uranium, and it may be that these two elements are simply concentrated in late-forming rocks of many different types (LARSEN Jr. and PHAIR, 1954).

The accumulation of thorium and uranium in residual fluids explains their presence in minerals of pegmatites and may partly explain the variation in their concentration from place to place within single plutons. Thus, the tendency of thorium and uranium to concentrate in the outer zones of some intrusions (INGHAM and KEEVIL, 1951) may be caused by the outward migration of essentially hydrothermal fluids. KRYLOV, (1956) finds that only uranium increases outward in intrusive bodies, with thorium decreasing from centre to periphery. Similarly, the variation in overall thorium and uranium contents of related intrusions may result from the escape of late-forming fluids from one body and their retention by another body. Redistribution of thorium and uranium among some minerals has also been indicated (TILTON *et al.*, 1954). Differences in the thorium and uranium contents of similar rocks may also, of course, be due to original differences in the magmas. Some studies (e.g. SENFTLE and KEEVIL, 1947) have indicated broad geographic provinces characterized by differences in the thorium and uranium contents of similar rock types. NEUERBERG (1956), among others, has discussed the evidence for uraniferous igneous provinces.

Silicic extrusive rocks. The average abundances of thorium and uranium in silicic extrusive rocks are in the range of 10–20 p.p.m. and 3–6 p.p.m. respectively. The average Th/U ratio is 3–5. The term "silicic extrusive rocks" is here taken to mean the aphanitic and glassy equivalents of the quartz-bearing, syenitic, and monzonitic, intrusive rocks.

The sites of thorium and uranium in extrusive rocks of any composition are difficult to determine. In intrusive rocks, much of the thorium and uranium appears to be concentrated in accessory minerals. Inasmuch as many of these minerals generally appear to form early during the crystallization of a magma, it might be expected that thorium and uranium would be incorporated in the first crystals formed from a lava and would thus be concentrated in a few grains. The major carriers of thorium and uranium in intrusive rocks, however, are the comparatively late-crystallizing accessory minerals such as monazite, xenotime, and allanite, and these minerals are probably absent from most extrusive rocks. Even minerals such as zircon, which probably crystallize earlier than monazite and xenotime, are less abundant or much finer grained in extrusive rocks than in intrusive equivalents. Consequently, in extrusive rocks the thorium and uranium might be expected to be widely dispersed, and this conclusion has been confirmed for some rocks by autoradiographic studies (ROGERS and ADAMS, 1957). In some cases the inability of thorium and uranium to enter lattices of the major minerals which crystallize from lavas (e.g. feldspars) and the absence of accessory minerals seems to cause the thorium and uranium to be concentrated in the residual magma and ultimately incorporated in the glass (EVANS and WILLIAMS, 1935). Other studies, however, have shown a rather uniform distribution of alpha-emitting elements among all of the mineral phases and glass (ROGERS and ADAMS, 1957) in both the basic and more acidic members of a suite of volcanic rocks. In extrusive rocks the thorium and uranium in quartz, feldspar, and ferromagnesian minerals may be attributed to submicroscopic inclusions of accessory minerals or may simply represent entrapment of the two ions by the rapid crystallization caused by extrusion.

Variations in the abundances of thorium and uranium in silicic extrusive rocks may be less than in intrusive rocks of equivalent composition. The wide variation in abundances exhibited by some intrusive bodies apparently does not occur in extrusive rocks. The average abundance of thorium and uranium in silicic extrusive rocks may be slightly higher than in intrusive rocks (uranium contents less than 1 p.p.m. are much rarer in extrusive than in intrusive rocks), but sampling difficulties make this conclusion only tentative. An average lower uranium content in intrusive rocks may indicate hydrothermal escape of uranium from a slowly crystallizing magma. In one studied sequence of volcanic rocks, the uranium content of the lavas is roughly proportional to the potassium content (ADAMS, 1955). If the alpha-count/fluorometric uranium analytical method is applicable to extrusive rocks, it appears that the Th/U ratio is essentially constant in these rocks despite variations in the total abundances of the two elements (ADAMS, 1955). Apparently, fractionation of thorium and uranium takes place less readily in extrusive than in intrusive rocks.

Basic intrusive rocks. The abundances of thorium and uranium in basic intrusive rocks (gabbros and diorites) are in the range of 0·5–5 p.p.m. and 0·3–2 p.p.m. respectively. The average Th/U ratio is 3–4.

The only abundant accessory minerals in basic intrusive rocks are the opaque ores (chromite, ilmenite, and magnetite) and apatite. None of these minerals commonly contain large amounts of thorium or uranium (though apatite contains some), and consequently it might be expected that the relatively small amount of radioactivity in these rocks would be rather uniformly distributed among the various constituents. This conclusion apparently is confirmed by

autoradiographic studies (PICCIOTTO, 1950). The small variation in abundances of thorium and uranium in basic rocks, as compared to the large variations in silicic intrusive rocks, is probably caused by the scarcity of hydrothermal fluids in the residual basic magma and consequently the absence of the broad redistribution of thorium and uranium which these fluids accomplish.

Basic extrusive rocks. The abundances of thorium and uranium in basic extrusive rocks (basalts and andesites) are in the range of 0·5–10 p.p.m. and 0·2–4 p.p.m. respectively. The average Th/U ratio is 3–7.

The thorium and uranium in studied basic volcanic rocks is roughly uniformly distributed among the various constitutents (ROGERS and ADAMS, 1957) or concentrated into the glassy phase (EVANS and WILLIAMS, 1935). The explanation for the distribution is the same as that given for silicic extrusive rocks. It is possible that the thorium and uranium apparently incorporated in the various major minerals of the rocks (plagioclase, pyroxene, etc.) are actually concentrated in submicroscopic grains of accessory minerals. It seems likely, however, that in quickly cooled lavas the thorium and uranium might be trapped in crystals in which they might not normally occur if equilibrium had been more nearly maintained during growth. The abundances of thorium and uranium in basic extrusive rocks are apparently not as variable as in granitic rocks.

Ultrabasic rocks. Available analyses of ultrabasic rocks (dunites and peridotites) show an extremely small amount of radioactive material. Uranium contents range up to approximately 0·1 p.p.m., and thorium is extremely scarce. What little radioactivity is present occurs in late-stage minerals such as kammererite (DAVIS and HESS, 1949), for analysed olivine grains have a uranium content in the range of 0·01 p.p.m. The low content of thorium and uranium in ultrabasic rocks confirms the general tendency for radioactive material to be concentrated in the more silicic rocks.

Alkaline rocks. Analyses of alkaline rocks indicate a great variability in the abundances of radioactive material. In some rocks the uranium content is as low as 0·1 p.p.m., and in other rocks the content is higher than in most granites. Some studies have shown a tendency for enrichment of radioactive material in alkaline rocks (LARSEN, Jr. and PHAIR, 1954).

Silicic pegmatites. The coarse grain size of pegmatites makes adequate sampling very difficult. The presence, and probable abundance, of thorium and uranium is shown by the occurrence of typical thorium- and uranium-bearing minerals such as monazite, uraninite, allanite, samarskite, and many others. The uranium-bearing minerals of pegmatites are described by PAGE (1950). The average thorium and uranium contents vary greatly from one pegmatite to another.

Summary

Based on the available data concerning the distribution of thorium and uranium among igneous rocks and minerals, a number of conclusions can be drawn. Some of these conclusions can only be tentative and certain details will undoubtedly have to be modified as more information becomes available.

Most studies have shown that the average Th/U ratio in igneous rocks is about 3·5. This ratio is found in rocks which are greatly different in average thorium and uranium contents and is the characteristic ratio of the very low concentrations present in the major rock-forming minerals like quartz and the

feldspars. Although this average ratio occurs in most representative suites of rocks, many individual specimens exhibit greatly different ratios. In granites, for example Th/U ratios ranging from less than 1 to about 25 have been observed. Nevertheless, the widespread occurrence of ratios of about 3·5 indicates that this is very close to the overall crustal ratio; wide deviations from 3·5 should probably be assigned to some special processes of rock formation.

Though the Th/U ratio in major rocks and minerals is commonly about 3·5, this ratio is not found in most of the accessory minerals in which thorium and uranium tend to be concentrated. In other words, a random aggregation of these accessory minerals in a rock or as fine inclusions in a major mineral like quartz generally exhibit a ratio of about 3·5, but the accessory minerals themselves deviate widely in both directions from this average ratio. The early-forming accessory minerals (zircon, apatite, and possibly sphene) commonly exhibit a Th/U ratio of about 1 or less. Later-crystallizing accessories, however, have Th/U ratios ranging from 100 (monazite) to 0·01 (xenotime). This pronounced fractionation of thorium and uranium in the late-stage minerals may be explained by the oxidation of tetravalent uranium to uranyl ion, which is markedly different chemically from tetravalent thorium. The ratio of 1 found in the early-crystallizing minerals, however, is not readily explained by simple oxidation of the uranium. Presumably, if oxidation of the uranium occurred during the early stages of magmatic crystallization, the thorium/tetravalent uranium ratio would be reduced, and minerals which incorporated these tetravalent ions would have a ratio greater than 3·5. The possibility that zircon and apatite can fractionate such chemically similar ions as tetravalent thorium and tetravalent uranium cannot be completely excluded, but the mechanism for such a fractionation is obscure. Rather than simple oxidation or crystal fractionation, complexes such as the tetravalent uranium-phosphate complex discussed above may play an important rôle in determining the ratio of thorium and uranium available to enter a receptive accessory mineral at any magmatic stage. It is also possible that most magmas have a Th/U ratio of about 1 at the start of their crystallization and that the final ratio of 3·5 is caused by the hydrothermal escape of uranium; however, it seems unlikely that a uniform ratio would be obtained by such a process and the evidence from basic rocks and lavas, where accessory minerals have not had an opportunity to crystallize with the thorium and uranium, indicates that normal, unassimilated magmas begin with a ratio of about 3·5. The importance of hydrothermal fluids in redistributing uranium, and even thorium to a certain extent, should not be minimized, and many of the great differences in the total uranium contents of comagmatic igneous rocks may be related to the movements of hydrothermal fluids.

On the assumption that most magmas start with a Th/U ratio of about 3·5, the following course of magmatic crystallization may explain the observed distribution of thorium and uranium in igneous rocks:

(1) Early-crystallizing minerals such as olivine from basic magmas incorporate almost no thorium and uranium, and the ultrabasic rocks consequently have barely detectable concentrations of these elements.

(2) During the crystallization of the normal minerals of basic rocks (pyroxene, calcic plagioclase, and apatite), the apatite may isomorphously incorporate small amounts of thorium and uranium. No mineral crystallizes from a basic magma with a marked concentration of thorium and uranium, and thus these

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two elements are ultimately rather uniformly dispersed among the constitutents of basic rocks.

(3) The failure of thorium and uranium to crystallize out of basic magmas leads to their enrichment in silicic magmas. Thus, the more silicic rocks (granites to tonalites) contain a relatively large amount of thorium and uranium. A significant fraction of the thorium and uranium is fixed by isomorphic substitution in certain accessory minerals. Zircon forms comparatively early and incorporates a moderate amount of thorium and uranium in about a 1:1 ratio. Much of the thorium and uranium, however, is concentrated in the residual magma, where it may ultimately be fractionated and fixed in minerals like allanite, monazite, and xenotime. A variable amount of thorium and uranium may also be fixed in the major minerals (commonly as inclusions) or along the grain boundaries and fractures. During the late stages of crystallization, hydrothermal fluids may redistribute the thorium or uranium, or they may escape to form hydrothermal veins and pegmatites. Hydrothermal uranium veins are usually markedly free of thorium, and it is possible that the uranium is transported as the simple or complexed uranyl ion and fixed by reduction to the tetravalent state. Hydrothermal thorium veins are also known (TWENHOFEL and BUCK, 1956), but their mode of origin is obscure.

The course of crystallization outlined above is applicable only to intrusive magmas. In extrusive lavas, rapid crystallization of all minerals commonly causes much more entrapment of thorium and uranium in the major mineral constituents. There is still some tendency for thorium and uranium to be concentrated in the glassy, uncrystallized portion of a cooled lava.

Thorium and Uranium in Metamorphic Rocks

In general the effects of metamorphism on the distribution of trace elements are not well known. The data regarding thorium and uranium are typical in this respect. ADAMS (unpublished) measured the alpha activities of the sixty-three specimens collected from the Littleton formation and described by SHAW (1954). The alpha activity, a function of the concentration of thorium and uranium combined, showed even less variation between the various grades of metamorphism than that found for zirconium by SHAW. Thus, there is some reason to believe that in the Littleton formation the metamorphism did not change the concentration of thorium and uranium; SHAW also found in the Littleton that the concentration of nearly all the trace elements he studied remained constant during this metamorphism.

KRYLOV (1956) studied the variations in the concentrations of thorium and uranium across the contact metamorphic zones of two granite stocks. In one, the data seemed to indicate a migration of uranium for a distance of up to 50 m into the metamorphosed zone. A similar migration has been observed by THURLOW (1956).

The thorium and uranium concentrations of twenty-five slates and schists and two marbles, as determined by the total alpha activity-fluorometric uranium method by PLILER (1956), and field determinations on thirty-two gneisses and anatectic rocks by HUSMANN (1956) are shown in Table 6. Also included are some measurements by COPPENS (1950) using autoradiographic methods. In general the data of Table 6 show that metamorphic rocks are not markedly different from average granite or corresponding sedimentary rocks in

Table 6. Thorium and Uranium in Metamorphic Rocks

Rock type	Number of Rocks	U p.p.m.	(U range)	Th p.p.m.	(Th range)	Th/U
From PLILER (1956)						
Marble	(2)	0·17	(0·11–0·24)	0·03	(0·02–0·04)	0·2
Slate	(14)	2·7	(1·2–6·1)	7·5	(3·0–25)	2·8
Phyllite	(7)	1·9	(1·0–2·7)	5·5	(3·8–16)	2·8
Schist	(4)	2·5	(1·8–2·9)	7·5	(4·3–26)	3·0
From HUSMANN (1956)						
Amphibolite	(3)	3·5	(2·6–4·1)	5	(2·4–7·8)	1·4
Biotite—hornblende paragneiss	(2)	2	(0·7–4)	27	(20–32)	13·5
Paragneiss	(4)	7	(6·5–9)	6·4	(1·7–10·1)	0·9
Granulite	(2)	4·9	(3·2–7)	21	(19–32)	4·3
Orthogneiss	(4)	3·6	(2·6–4·5)	5·5	(2·6–8·9)	1·5
Metatectite	(4)	4·8	(3·3–7·1)	22	(14·3–27)	4·6
Diatectite	(4)	11·2	(7·2–11·9)	3	(0·5–10·3)	0·3
Cordierite gneiss	(1)	5·8	(3·6–7·8)	21·8	(14·8–29)	3·8
Orthoclase porphyroblasts	(1)	45	(35–57)	67·7	(26–100)	1·5
Kinzigite	(1)		(–0·4)	7	(5·6–7)	
From COPPENS (1950)						
Gneiss	(3)	8·2	(4·5–15)	20·3	(11·0–37·5)	
Granulite	(5)	4·9	(2·5–6·5)	12·2	(6·2–16)	

their thorium and uranium content. There is, however, some indication that the Th/U ratio may be lower in the metamorphic rocks. If further data support this trend it may mean that uranium is more likely than thorium to be introduced into rocks by metamorphic processes.

It would be of great interest to compare the distribution of thorium and uranium in the minerals of metamorphic rocks relative to their distribution in magmatic rocks. Only a few data are yet available on this subject. HURLEY and FAIRBAIRN (1957) analysed a few sphenes from metamorphic rocks and found concentrations not unlike those for magmatic sphenes (215–1400 p.p.m. U, 170–2400 p.p.m. Th, and Th/U of 0·7–2·5). The high uranium and thorium values found by HUSMANN (Table 6) in orthoclase porphyroblasts is correlated with a 0·1 per cent concentration of allanite.

Thorium and Uranium in Sedimentary Rocks, the Hydrosphere, the Biosphere, and the Atmosphere

Studies in the last few years have resulted in more quantitative concepts regarding the mobilization, transportation, and deposition of the thorium and uranium originally present in primary igneous rocks that have been weathered and

eroded. In sedimentary rocks, the early and excellent determinations of JOLY (1910), together with the determinations and geochemical theory of GOLDSCHMIDT (1954) gave rise to a number of concepts that were confirmed for the most part by the subsequent data and discussions summarized by MCKELVEY and NELSON (1950), RANKAMA and SAHAMA (1950), BELL (1954), and by MCKELVEY *et al.* (1955). However, the number of published analyses on the thorium and uranium contents of sedimentary rocks and natural waters has increased many-fold in the last two years, and these data, as summarized in the following section, provide a still firmer basis for a discussion of this phase of the geochemistry of these elements.

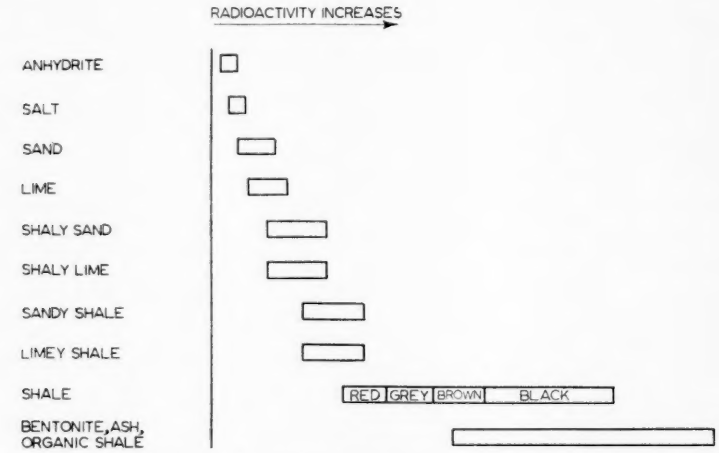

Fig. 1. Relative radioactivity range of sedimentary rocks. (After MERCIER, 1950, *Subsurface Geologic Methods*, LeRoy, Colorado School of Mines.)

Sedimentary rocks. An important source of information about the distribution of thorium and uranium in common sediments is provided by the millions of feet of gamma-ray logging done in connexion with petroleum exploration. Care must be used in the evaluation of these data because: (1) potassium-40 contributes an important and variable fraction of the total gamma-ray flux detected; (2) a variety of detectors, including Geiger–Müller tubes, ionization chambers, and scintillation counters, are used; (3) many of the logs are only relative, not absolute, with the base-line set on the least active rock in the section (usually a limestone with low shale content); (4) carbonate sections are the most frequently logged, although all sedimentary rock types are well sampled. Offsetting the above reservations are the facts that the gamma-ray logging data record the radioactivity from a tremendous volume of sedimentary rock and that these data provide relative upper limits on the combined concentration of thorium and uranium. MERCIER (1950), among others, has recently summarized gamma-ray logging techniques, and Fig. 1 is a reproduction of his summary of the relative gamma-ray activity ranges of common sedimentary rocks. Figure 1 is based upon laboratory data and the experience gained in logging over 15,000 wells. It should be noted that if spectral gamma-ray logs

(see ADAMS and WEAVER, 1958) ever become widely used, they will contribute much quantitative information on the distribution of thorium, uranium, and potassium, because these spectral gamma-ray logs resolve the separate contributions of these gamma-emitters, thus giving a direct measure of the concentration of each of the three elements involved.

The qualitative ranges of total gamma-ray activity shown in Fig. 1 are of considerable use for comparison with the following quantitative data available on the thorium and uranium contents of sedimentary rocks. ADAMS and WEAVER (1958) have recently compiled such quantitative data, drawing largely from three sources: (1) their own measurements on individual rocks and a few small aggregates; (2) the measurements of BARANOV *et al.* (1956) on large aggregate samples of Russian rocks; and (3) various scattered studies consisting of much smaller numbers of rocks where both thorium and uranium were determined. There is substantial agreement to well within estimated errors between the values obtained from these three sources, although a wide variety of analytical techniques were employed. Subsequent to the compilation of ADAMS and WEAVER (1958), additional data on orthoquartzites (MURRAY and ADAMS, 1958) and on bauxites (ADAMS and RICHARDSON, 1957) have become available. Table 7 is a summary of the data on sedimentary rocks and is largely a modification with additions of the compilation of ADAMS and WEAVER (1958). The categories in Table 7 are established arbitrarily so as to facilitate later discussion, but numerous reservations must be made regarding the classification of some samples and the integrity of each category. The degree to which the samples are adequate and representative must also be considered in each of the following categories from Table 7.

Common shales. Shale material forms, on a computed basis, about three-quarters of all sediment (PETTIJOHN, 1957). This predominance of weight, together with the observations that common shale averages higher in thorium and uranium than sandstones and carbonate rocks, make common shales a dominant term in the present discussion. The mean thorium content of 12 ± 1 p.p.m. for common shale is believed to be substantially correct because this range includes the average (13 p.p.m.) of fifty-two determinations on individual American shales reported by ADAMS and WEAVER (1958), as well as the average (11 p.p.m.) of fifteen determinations on aggregates representing 4795 individual Russian shales (BARANOV *et al.*, 1956). The range of thorium values given in Table 7 is strongly influenced by one or two values that may not represent common shale material; it should be noted that over 90 per cent of all thorium values fall between 8 and 18 p.p.m. (ADAMS and WEAVER, 1958).

As is the case with thorium, the average uranium content of $3{\cdot}7 \pm 0{\cdot}5$ p.p.m. in Table 7 gives a range that covers the average values of both BARANOV *et al.*, (1956) and of ADAMS and WEAVER (1958). The former report 4·1 p.p.m. and the latter 3·2 p.p.m. for the average of a common shale. Here again, the range of uranium values is greatly influenced by a few samples that may not represent common shale material; well over 90 per cent of the uranium values fall within 1·5 and 5·5 p.p.m.

The average value for the Th/U ratio of common shales is given in Table 7 as $3{\cdot}8 \pm 1{\cdot}1$, which is relatively a much wider range than the ranges stated for thorium and uranium. ADAMS and WEAVER (1958) found an average Th/U ratio of 4·9, whereas BARANOV *et al.* (1956) report 2·7. This difference may be

Table 7. Average Values and Ranges for Thorium, Uranium, and Th/U *Ratios in Sedimentary Rocks*

	Thorium (p.p.m.)		Uranium (p.p.m.)		Th/U ratio		Number of samples	Number of determinations
	Average	Range	Average	Range	Average	Range		
Clastic rocks								
Common shales	12 ± 1	2–47	3·7 ± 0·5	1–13	3·8 ± 1·1	1–12	4847	75
Orthoquartzites	1·7 ± 0·1	0·7–2·0	0·45 ± 0·05	0·2–0·6	4·0 ± 0·8	1·8–5·8	18	18
Black shales	—	2·8–28	—	1·4–80	—	0·07–12	350	18
Residual rocks								
Bauxites	42	8–132	8·0	3–27	6·9	1·5–22	26	26
Bentonites	24	6–44	5·0	1–21	5·8	1·0–21	69	69
Precipitated rocks								
Carbonate rocks	1·7 ± 0·7	0·1–7	2·2 ± 0·1	0·1–9	1 ± 0·3	0·1–6·5	6045	103
Halite	—	0·4–0·5	—	0·1–0·2	—	1–5	3	3
Anhydrite	—	0·15	—	0·1	—	1·5	1	1
Phosphate rock	—	3·9	—	245	—	0·02	1	1
Chert	—	0·1–1·6	—	1·9–3·3	—	0·01–0·9	2	2

due to the different analytical techniques used in the two investigations, but the excellent agreement on the uranium and thorium contents of carbonate rocks (see section on carbonate rocks below) would suggest that the difference between the two values for average Th/U ratios is due primarily to the samples selected to represent common shales. The large number of samples represented in the aggregate samples of BARANOV *et al.* (1956) would indicate that their value may be closer to that of common shale. It is hypothesized that the average Th/U ratio value of ADAMS and WEAVER (1958) may be somewhat biased by the inclusion of too many samples of well-weathered, continental material with high thorium contents and high Th/U ratios (see section below on the separation of thorium and uranium in sedimentary processes).

Orthoquartzites and other sandstones. The available data on sandstones are extremely limited. ADAMS and WEAVER (1958) analysed one graywacke (1·2 p.p.m. uranium and 3·0 p.p.m. thorium), one arkose (0·9 p.p.m. and 4·5 p.p.m.), and one orthoquartzite (0.3 p.p.m. and 1·0 p.p.m.). EVANS and GOODMAN (1941) analysed one sandstone (0·86 p.p.m. uranium and 5·4 p.p.m. thorium). MURRAY and ADAMS (1958) analysed sixteen orthoquartzites, yielding the bulk of the data given in Table 7; they also found that the thorium and uranium in their samples were in inclusions in the quartz with separate heavy mineral grains like zircon and monazite making a negligible contribution. The lack of data precludes any discussion of arkoses and graywackes beyond the tentative expectations that: (1) the arkoses will tend to be similar to the orthoquartzites, because the thorium and uranium contents of quartz and feldspar are similar (see Table 5); and (2) the graywackes will tend to be similar to the average of common shales or primary igneous source rocks. The values given for average orthoquartzite in Table 7 are probably much more representative than is indicated by the small number of samples and the fact that 10 of the 16 samples are beach sands from Galveston, Texas. The very small range in the values together with the geologic observation that orthoquartzites tend to represent well-mixed quartz from widely different sources indicate that the values in Table 7 may be fairly representative of both orthoquartzites and terrestrial quartz. Much of the observed variation in the thorium and uranium determinations can be assigned to analytical errors in determining such low concentrations.

ADAMS and WEAVER (1958) attempted to calculate the average thorium and uranium contents of sandstones from geochemical balances, but the errors, particularly in the relative proportions of the major sediments, are large (see geochemical balances below). MURRAY and ADAMS (1958) also considered the average content of orthoquartzites, especially as regards the effect on the average of placer sands containing unusual amounts of minerals like zircon and monazite (see Table 5 and discussion on geochemical balances below). In a strict sense, the values for orthoquartzites given in Table 7 should be considered the modes or most frequent values. However, the limited areal extent of such placer sands containing unusually high concentrations of thorium and uranium (see *Proc. International Conf. on Peaceful Uses of Atomic Energy*, Vol. 6 (1956)) and the great rarity of such rocks in the subsurface (see Fig. 1), would suggest that the average or mean for orthoquartzites is only slightly higher than the figures given in Table 7.

Black shales. The unusually high radioactivity and uranium content of

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certain marine black shales, e.g., the Chattanooga in the U.S.A. and the Dictyonema in Scandinavia, have long been known and used in gamma-ray logging (see Fig. 1 and, among others, SWANSON (1956), COPPENS (1953), BATES and STRAHL (1957)). ADAMS and WEAVER (1958) found that the thorium content in marine black shales was essentially the same as that in common shales except in cases where a large percentage of carbonaceous or carbonate material diluted the normal shale material (see Table 6). Three of the four continental black shales analysed by ADAMS and WEAVER (1958) had high thorium contents (19, 21 and 24 p.p.m.) and nominal uranium contents (2·0, 3·6 and 4·8 p.p.m.). Thus, a distinction may exist between marine and continental black shales in regard to their thorium and uranium content. The distribution and origin of the uranium in the Chattanooga shale has been intensely investigated (see *Proc. International Conf. on Peaceful Uses of Atomic Energy*, Vol. 6 (1956)). From these investigations it is clear that the uranium is very dispersed and in variable concentration (10–100 p.p.m.), but it is uniformly much higher than in common shales. The alpha activity data of KRUMBEIN and SLACK (1956) on a black shale in a Pennsylvanian cyclothem in Illinois indicate that the thorium and uranium concentrations in such a shale can remain relatively constant for distances of up to several hundreds of miles.

Bauxites and continental shales. The data on continental shales are sparse. ADAMS and WEAVER (1958) analysed twelve red and yellow continental shales and found that their thorium content was in the general range of common shales though their uranium content tended to be lower (1–2 p.p.m.). ADAMS and RICHARDSON (1957) analyzed twenty-six commercial or nearly commercial bauxites and found their average thorium content to be 42 p.p.m., about three times that of common shales. The average uranium content of these bauxites, 8 p.p.m., was over twice that of common shales. Nearly all of the bauxites had high Th/U ratios, and there were indications that the rock from which the bauxite formed greatly influenced its thorium and uranium content; thus, limestones gave rise to bauxites with lower thorium and uranium contents and lower Th/U ratios, whereas bauxites derived from acid igneous rocks were much higher in all three values. Material balances and petrographic studies of the raw bauxite and the products of alumina plants indicated that at least 90 per cent of the thorium and uranium in the Arkansas and Surinam bauxites is contained in resistate minerals like zircon and monazite.

Bentonites. Like certain marine black shales, bentonites have long been known to be unusually radioactive, and this property has been used in gamma-ray logging (see Fig. 1). HAMILL (1957) (quoted in ADAMS and WEAVER, 1958) analysed 69 samples of bentonite (altered volcanic ash), largely from the Ordovician of the Appalachian region of the U.S.A. He found that the high radioactivity was due, in varying degrees, to the higher concentration of all three sources of natural gamma-radiation (thorium, uranium, and potassium). On the average the bentonites had about twice as much thorium and uranium as common shales, and as a rule they had higher Th/U ratios.

Carbonate rocks. In several respects carbonate rocks may be considered the best known sedimentary rocks as regards their thorium and uranium contents (see Table 7). ADAMS and WEAVER (1958) summarized the data from various workers on 6045 carbonate rocks, representing for the most part analyses of

large aggregate samples. The uranium content of these samples ranged from less than 0·5 p.p.m. to 9 p.p.m. with both the mean and median being about 2 p.p.m. The mean uranium content of carbonate rocks is about 2·1 p.p.m. with close agreement between various workers using different analytical techniques on samples drawn almost entirely from North America and European Russia. ADAMS and WEAVER (1958) reported that an average of 80 per cent of the uranium in a carbonate rock can be brought into solution by dissolving in weak acid. They concluded that the uranium is either in the carbonate lattice or on the grain surfaces. ADAMS and LEWIS (to be published) found that in a single thin

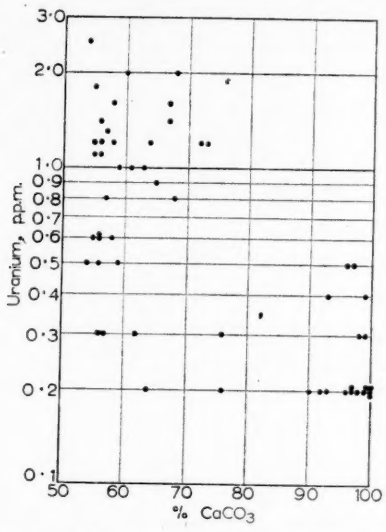

FIG. 2. Uranium vs. $CaCO_3$ through a limestone to dolomite transition.

carbonate bed containing a limestone to dolomite transition, the average uranium content in the limestone samples was less than that in the dolomites (see Fig. 2). They also found that the dolomite samples exhibited a greater range in uranium concentration, being as high or higher than the limestone samples (see Fig. 2).

The average thorium content of the 6045 carbonate rocks cited above is less than 2 p.p.m. Both BARANOV *et al.* (1956) and ADAMS and WEAVER (1958) found that the thorium content of a carbonate rock is primarily a function of the siliceous clastic (essentially shale) content. Thus, the purer carbonate rocks are found to have less than 0·1 p.p.m. thorium, and a rock made up of equal portions of limestone and shale tends to have a thorium content of about 6 p.p.m., one-half that found in common shales. This relationship was further confirmed by the observation of ADAMS and WEAVER (1958) that the clastic insoluble residue of a limestone had the thorium and uranium concentrations found in common shale. ADAMS and LEWIS (to be published), despite analytical uncertainties owing to the low concentrations present, concluded that thorium was unique among some twenty trace elements studied in that its concentration

over a limestone to dolomite transition did not exhibit any change in the average or range of values (see Fig. 3).

Halite and anhydrite. The quantitative data on these evaporites is limited to a few samples, but these data do provide some quantitative concept of the upper limits of the thorium and uranium contents of these least radioactive rocks (see Fig. 1 and BELL, 1956).

Phosphate rocks. Although there is only one thorium determination listed in Table 7, the unusually high uranium content of many phosphate rocks has

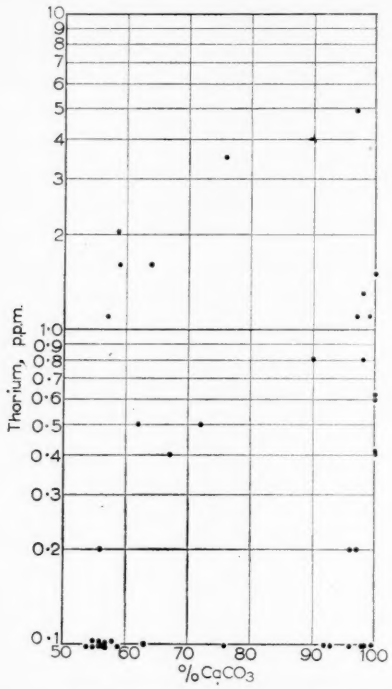

Fig. 3. Thorium vs. $CaCO_3$ through a limestone to dolomite transition.

been the subject of intense investigation (see, e.g. CATHCART, 1956; MCKELVEY, 1956; DAVIDSON and ATKIN, 1953; *Proc. International Conf. on Peaceful Uses of Atomic Energy*, Vol. 6, 1956). It is clear that these rocks usually have very low Th/U ratios as a result of their generally high uranium concentrations.

The hydrosphere. The amounts of thorium and uranium in the hydrosphere are extremely low, their normal concentrations being 0·001 p.p.m. or less. Determinations of uranium in natural waters have become routine (see SMITH and GRIMALDI 1954; ADAMS, 1954a; and FIX, 1956), but our knowledge of thorium concentrations as yet is based only on upper limits and deductions. The numerous measurements of radium and emanation in the hydrosphere reported throughout the literature are not of great use in calculating uranium and thorium concentrations because it is impossible to make any equilibrium assumptions for the radio-elements in solutions.

HOLLAND and KULP (1954) have calculated the geochemical balance for uranium in the hydrosphere, and KOCZY (1956) has summarized the hydrosphere geochemistry of both thorium and uranium.

Thorium and uranium in continental waters. The amounts of thorium and uranium in hot springs and volcanic gases are uncertain. Except locally, the contribution of juvenile waters to the thorium and uranium of the hydrosphere is probably not important; HOLLAND and KULP (1954) calculate that weathering of surface rocks alone can account for the uranium in rivers. Although many hot springs are found to be high in radium, actual measurement shows that the concentration of uranium in such waters is quite low, less than 0·007 p.p.m., according to FIX (1956). Studies by HOFFMANN (1940, 1941c) indicate that sulphur springs may be higher in uranium than other springs. Little is known about thorium in thermal waters, but its abundance would be expected to be much lower. At certain periods and times the amount of uranium in hydro-thermal solutions may have been quite high according to WRIGHT and SHULHOFF (1956).

Ground waters circulating through mineralized aquifers are known to dissolve uranium up to a concentration of a few tenths of a part per million (FIX, 1956; JUDSON and OSMOND, 1955; and DENSON *et al.*, 1956), but this is far above average for fresh waters of intermediate pH.

A value of 0·0001 p.p.m. uranium has been given by FIX (1956) as a regional average for natural waters in the U.S.A. and Alaska. In areas affected by mineralized dispersion auras, he reports that the average may be 0·00080 p.p.m. Other regional averages and specific determinations are listed in Table 8. Also included in Table 8 are two values for average river water made on the basis of

Table 8. Thorium and Uranium in Continental Waters

Concentration (p.p.m.)	Location	Reference
Thorium		
0·00001	River water, by calculation	KOCZY (1956)
Uranium		
< 0·007	Thermal springs	FIX (1956)
0·00002–0·048	Thermal springs, Erzgebirge	HOFFMANN (1940, 1941c)
0·093	Sulphur spring, Erzgebirge	HOFFMANN (1940, 1941c)
0·0001	U.S.A., Alaska, regional average	FIX (1956)
0·0005–0.003	Colorado Plateau	FIX (1956)
0·0023–0·010	Texas ground water	JUDSON and OSMOND (1955)
0·0008	Wisconsin and Illinois ground waters	JUDSON and OSMOND (1955)
0·0002	Washington	ILLSLEY (1957)
0·000026	Three N. American rivers	RONA and URRY (1952)
0·0005	Baltic region, igneous drainage	KOCZY *et al.* (1957b)
0·001–0·013	Baltic region, sedimentary drainage	KOCZY *et al.* (1957b)
0·00009–0·0011	River water, by calculation	HOLLAND and KULP (1954)
> 0·00015	River water, by calculation	This paper
0·0048	Great Salt Lake, Utah	STEWART and BENTLEY (1954)
0·020–0·200	Mineralized aquifer	FIX (1956)
0·010–0·250	Mineralized aquifer	DENSON *et al.* (1956)
0·100–0·460	Mineralized aquifer	JUDSON and OSMOND (1955)

geochemical balances, one by HOLLAND and KULP (1954) and one by the present authors (see section on geochemical balances). These theoretical values are seen to be in fair agreement with regional averages as determined by analysis.

The total concentration of uranium is about the same in ground and surface waters of a given area, but waters in arid regions seem to have a higher concentration of uranium than do waters in humid regions (see data of JUDSON and OSMOND, 1955; and FIX, 1956). KOCZY *et al.* (1957b) report that in the Baltic region rivers draining sedimentary rock areas have twice the uranium concentration found in rivers that drain igneous rock areas.

The amount of uranium in true solution may be only a fraction of the total uranium concentration of river water, the remainder being held on the surface of suspended particles (ADAMS, quoted in HOLLAND and KULP, 1954) or in suspended resistates.

The amount of thorium in river water has not been measured directly. KOCZY (1956) estimates that the contribution to the ocean by river water requires a concentration of about 0.00001 p.p.m. in river water. Comparing this figure with the uranium in solution, it appears that the Th/U ratio in river water is not larger than 0·1 to 0·01. Since the total ratio of the thorium and uranium transported to the sea by rivers (in solution, suspension, and bottom load) is probably about the same as the ratio in source rocks and shales (3·5), it may be hypothesized that thorium to a greater extent than uranium is carried to the sea on hydrolyzates and in resistates.

Thorium and uranium in the sea. KOCZY *et al.* (1957a) give the value for uranium in the sea as 0·001 to 0·006 p.p.m. and thorium as less than 2×10^{-5} p.p.m. The Th/U ratio in sea-water is less than 10^{-2}. The uranium value is fairly certain. The determinations that have been reported by FØYN *et al.* (1939), G. KOCZY (1950), NAKANISHI (1951), SMITH and GRIMALDI (1954), and STEWART and BENTLEY (1954) are all within the range given by KOCZY (see Table 9).

Table 9. Thorium and Uranium in Sea-Water

Concentration (p.p.m.)	Location	Reference
Thorium		
$< 5 \times 10^{-4}$	Scandinavian waters	FØYN *et al.* (1939)
4×10^{-8}	Scandinavian waters	KOCZY (1956)
$< 2 \times 10^{-5}$	Scandinavian waters	KOCZY *et al.* (1957a)
Uranium		
0·00036–0·0023	Scandinavian waters	HERNEGGER and KARLICK (1935)
ave. 0·0015	Atlantic, Pacific	FØYN *et al.* (1939)
0·0011–0·0015		G. KOCZY (1950)
0·0003–0·0010	North Atlantic	RONA and URRY (1952)
0·0025	Pacific	STEWART and BENTLEY (1954)
0·0028	Pacific	NAKANISHI (1951)
0·00115	Atlantic	SMITH and GRIMALDI (1954)
0·00315	Gulf of Mexico	SMITH and GRIMALDI (1954)
0·0031–0·0035	Atlantic, Pacific, Gulf of Mexico	RONA *et al.* (1956)
0·0008–0·0059	Baltic Sea	KOCZY *et al.* (1957b)

RONA *et al.* (1956), using an isotope dilution method, report a slightly higher value. Variations in the uranium content of the sea may be related to salinity (FØYN *et al.*, 1939; KOCZY *et al.*, 1957b) or to local redox potential (KOCZY *et al.*, 1957b). The thorium estimate is uncertain. Attempts at direct measurement have failed because the concentrations fell below the limit of detection (KOCZY *et al.*, 1957a).

Both the thorium and uranium carried to the sea by rivers have been considered to be removed almost quantitatively in shelf sediments (HOLLAND and KULP, 1954; KOCZY, 1954). In addition to the amounts of these elements deposited with resistates and hydrolysates on the shelf, a certain addition of uranium from sea-water may occur during sedimentation, possibly by the action of marine organisms (KOCZY, 1956), by chemical reduction (MCKELVEY *et al.*, 1955), or by coprecipitation (ADAMS and WEAVER, 1958). HOLLAND and KULP (1954) calculate that such addition may comprise one third of the 3 p.p.m. uranium in an average shelf sediment. ADAMS and WEAVER (1958) indicate that 80 per cent of the uranium in limestone (U of 2·2 p.p.m.) may be coprecipitated.

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In the deep sea, the rate of removal of uranium and thorium is very slow. Pelagic red clay, which seems to be forming at a rate of about 1/2 cm per 1000 years, contains about 5 p.p.m. thorium and about 2 p.p.m. uranium (PICCIOTTO and WILGAIN, 1954; see also BARANOV and KUZ'MINA, 1957). KOCZY (1954) estimates that the current inventory of uranium in the sea could be replaced by influx from rivers in a period of some 10^4 years. The period required to replace thorium would probably be even shorter. This would indicate that the oceans are saturated with respect to these two elements and that their concentrations may not have changed appreciably in the period of geologic time discussed by RUBEY (1951) in his history of sea-water. HOLLAND and KULP (1954) estimate a variation of less than 20 per cent. KOCZY (1956), however, suggests that the action of organisms, especially in the deposition of uranium, may have changed the concentrations by as much as a factor of three.

Of special interest to geochronologists is the behaviour of the short-lived thorium-230 isotope, ionium ($T_{1/2} = 80{,}000$ years), whose concentration in sea-water is estimated to be about 1/500 of thorium-232 (KOCZY, 1956). Intensive studies are being made to determine how ionium is concentrated in sediments relative to the other members of the uranium-238 series. Such studies should augment present knowledge of the thorium and uranium geochemistry in the sea.

The Biosphere

Organisms may concentrate thorium or uranium in certain of their tissues, for example the thyroid of animals or the leaves of plants, and the possibility that one or both elements may be essential trace elements (micronutrients) in some organisms is mentioned by RANKAMA and SAHAMA (1950). The manner of distribution and concentration of uranium in organic material has been studied extensively by HOFFMANN (1941a, 1941b, 1943a, 1943b), and the extraction of uranium from aqueous solutions by organic matter has been studied by MOORE (1954). The distribution of thorium in organisms is just beginning to be studied now that more satisfactory analytical procedures have been developed. As yet, any unique and essential metabolic rôle of thorium or uranium in any organism has not been demonstrated.

The geologic occurrence of thorium may in some instances bear a relation to organic or carbonaceous material (see Table 10). GOLDSCHMIDT (1954) reports

Table 10. Some Measurements of Thorium and Uranium in Organic and Associated Materials

Material	Concentration (p.p.m.)	Reference
Thorium		
Algae	not found	VINOGRADOV (1953)
Globigerina ooze	0·11–0·15	G. KOCZY (1950)
Alum shale	0·6–1·9	F. KOCZY (1949b)
Fish skeleton	4500 p.p.m.	BOWIE and ATKIN (1956)
Coal ashes	100 p.p.m.	GOLDSCHMIDT (1954)
Uranium		
Cattle bones	0·013	HOFFMANN (1941a)
Fresh water algae	9	HOFFMANN (1941b)
Various plants	0·1–34	HOFFMANN (1943a, 1943b)
Thyroid	10	HOFFMANN (1943b)
Plants in mineralized ground	1–100	CANNON and KLEINHAMPL (1956)
Black mud of fjord	13–60	STROM (1948)
Crude oil	$< 0{\cdot}064$	ERICKSON *et al.* (1954)
Asphalt	up to 30,000	ERICKSON *et al.* (1954)
Lignites	up to 200	DENSON *et al.* (1956)
Alum shale	20–200	F. KOCZY (1949b)
Chattanooga shale	10–350	SWANSON (1956)
Coral limestone	3–5·5	BARNES *et al.* (1956)
Fish skeleton	2700	BOWIE and ATKIN (1956)
Uraniferous coal ashes	330	BREGER and SCHOPF (1955)

100 p.p.m. thorium in coal ashes, and BOWIE and ATKIN (1956) found even higher concentrations in skeletal remains of fish. In the deep sea, shell material is slightly higher in thorium than red clay (KOCZY, 1949a). On the other hand, in the uraniferous alum shales of Sweden, the amount of thorium (1·9 p.p.m.) has a higher correlation with clay content than with organic matter in the samples (KOCZY, 1949b).

The common geologic association of uranium with carbonaceous sediments and organic matter is well known. Examples of this association are to be found among the marine black shales, lignites, asphalts, petroleum, and coral limestone. Among the authors who have discussed this subject are RUSSELL (1945), TOMKEIEFF (1946), MCKELVEY and NELSON (1950), and ERICKSON *et al.* (1954). It is not yet clear to what extent this association is due to the action of living organisms, and to what extent it is due to chemical action by the carbon or sulphur in organically derived material.

The three most studied types of uraniferous-organic geologic deposits are black shales, petroleum, and coal. In black shales with high uranium content (up to 350 p.p.m., see Table 10) the evidence that the organic material and uranium are contemporaneously deposited and probably related is good (MCKELVEY and NELSON, 1950; and SWANSON, 1956). In petroleum and asphalt,

the evidence is uncertain. Asphalts are higher in uranium than petroleum (ERICKSON, *et al.*, 1954), and the uranium in crude oil does not seem to be correlated with nitrogen content, as would be expected if it were present as a uranium–porphyrin complex (HYDEN, 1956). In coals and lignites, where high uranium content is the exception, most uranium seems to be secondary and related to porosity and uraniferous ground waters (DENSON *et al.*, 1956).

Recent studies have been concerned with high thorium and uranium values in marine skeletal material (BOWIE and ATKIN, 1956; and ARRHENIUS *et al.*, 1957). Indications are that such organic debris tends to pick up many trace metals from sea-water after deposition. On the other hand, biogenous opal (radiolaria and diatoms) is less radioactive than other types of sediment (ARRHENIUS *et al.*, 1957).

In summary, though certain animals and plants are known to contain thorium and uranium in amounts somewhat greater than those found in sea-water and normal sediments, concentrations of these elements solely by accumulation of dead organic matter has not been shown. BREGER and DEUL (1956) in a review of the organic geochemistry of uranium state:

". . . it is evident that neither plants nor animals normally contain appreciable percentages of the element. Secondary process must, therefore, be responsible for the introduction of uranium into carbonaceous deposits."

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The Atmosphere

One would not expect to find much thorium and uranium in the atmosphere under normal conditions, and no attempt at these measurements has been reported. However, data on the daughter elements of thorium and uranium series in the atmosphere have been collected over a period of 50 years (BLANC, 1907; ANDERSON *et al.*, 1954; FEDAROV and BARANOV, 1956). STOUT *et al.* (1956) studied the radioactive leads in air and found that both lead-212 of the thorium series and lead-214 of the uranium series are important components of the radioactivity. The apparent atmospheric source in each case is the emanation parent: Em^{222} (radon) of the uranium series, and Em^{220} (thoron) of the thorium series. The half life of Em^{222} (radon) is greater (3·8 days) than that of Em^{220} (thoron) (55 sec), and one might expect that Em^{222} (radon) would escape in greater amounts into the atmosphere. However, other factors such as mechanism of escape and method used for collection and measurement make the contribution of the thorium series of comparable importance.

The amount of radioactivity in the air has been observed to be correlatable with atmospheric conditions by STOUT *et al.* (1956), with geology by REITER (1956), and with altitude by WILKENING (1953). Possibly the source of the radioactive gases and leads in air is in part radium, uranium and thorium in the dust of the atmosphere.

At altitudes less than 500 ft above the ground, gamma-ray activity from ground sources can be measured, a fact which is the basis for air-borne radioactivity surveying (see STEAD, 1956; GREGORY, 1956; and MOXHAM *et al.* 1957). The effect on such aerial data of airborne radio-elements is not certain but is presumably small.

The determination of the thorium and uranium in the dust of the atmosphere would be of interest in the above connexion and also in estimating the importance of aeolian transport of thorium and uranium, particularly as it relates to the

thorium found in evaporite deposits, e.g. halite, and deep-sea sediments, e.g. manganese nodules.

Geochemical Balances

Geochemical balances in which the thorium and uranium in the average of all the igneous rock that has been weathered and eroded is balanced against the thorium and uranium found in all the sediments provide, within limits, an internal check on the average abundance data presented in the preceding sections. POLDERVAART (1955) and PETTIJOHN (1957) have recently reviewed the several difficulties involved in estimating the relative proportions of the major rock types involved in such geochemical balances. Table 11 presents geochemical balances for thorium and for uranium. Because of the close geochemical similarities between zirconium, thorium, and uranium (see page 308), DEGENHARDT's (1957) recent geochemical balance for zirconium is included in Table 11, together with Zr/Th and Zr/U ratios. Considering the several uncertainties, the uranium balance can be considered reasonably close, but the thorium balance is not as close as might be desired. The possible reasons for this lack of balance may be sought in the uncertainties discussed below that apply to both the thorium and the uranium balances.

A closer balance for thorium could be achieved by reducing the estimated average thorium concentration of 11·4 p.p.m. for all the igneous rock that has been weathered and eroded. A strong possibility for such a reduction lies in a lower estimate for the thorium content of the average basic igneous rock, because the data on such rocks are among the most limited (see Table 4). Another possibility for reduction lies in substantially increasing the proportion of basic igneous rock taken, but many workers (VOGT, 1931; POLDERVAART, 1955; and DEGENHARDT, 1957; among others) agree that only about 20 per cent of the igneous source rock is basic. A third and substantial possibility lies in a slight reduction to about 12 p.p.m. in the estimate for acid igneous rocks.

A closer balance in thorium could also be achieved by increasing the estimate for the thorium content of the average sediment. It is unlikely that the shale proportion could be increased very much, because the geochemical proportion of about 80 per cent is already much higher than the proportion found by the measurement of stratigraphic sections and assumes a significant loss of shale material to the deeper ocean basins (see PETTIJOHN, 1957). If continental, high thorium, shales are not adequately represented in the shale average of 12 $\pm$ 1 p.p.m., this figure may be slightly too low, resulting in part of the imbalance. The carbonate rocks are so low in thorium and their contribution to the total so small that no significant possibility for adjustment exists in this term. Furthermore, the conclusions of ADAMS and WEAVER (1958) that all of the thorium and only about 20 per cent of the uranium in the average carbonate rock is contained in the detrital, essentially shale, residue indicate that for the detrital residue: (1) the average thorium content is about 13 p.p.m.; (2) the average Th/U ratio is 3·9; (3) the average Zr/Th ratio is 11; and (4) the average Zr/U ratio is 48. All of these latter values are very close to those for average shale, thus providing additional reasons for believing that the average shale values are essentially correct.

There can be little question that the average concentration of thorium in sandstones used in Table 11 is too low. For one thing, this figure is based

Table 11. Geochemical Balances for Thorium, Uranium, and Zirconium

	Relative proportions	Thorium concentration (p.p.m.)	Thorium contribution (p.p.m.)	Uranium concentration (p.p.m.)	Uranium contribution (p.p.m.)	Zirconium concentration (p.p.m.)*	Zirconium contribution (p.p.m.)*	Zr/Th	Zr/U
Igneous source rock									
Acidic	80	13·5 ± 1·5	10·8	3·5 ± 0·5	2·8	—	—	—	—
Basic	20	3·0 ± 2·0	0·6	1·0 ± 0·5	0·2	—	—	—	—
Total	100		11·4 ± 2		3·0 ± 0·6		156	13	52
Sedimentary rocks									
Shales	80	12 ± 1	9·6	3·7 ± 0·5	3·0	160	127·4	13	43
Sandstones	12	1·8 ± (?)	0·2	0·5 (?)	0·06	220	26·2	120	440
Carbonate	8	1·7 ± 0·7	0·1	2·2 ± 0·1	0·17	19	1·5	11	8
Total	100		9·9 ± 1		3·2 ± 0·4		155	16	48

* Data from DEGENHARDT (1957).

solely on orthoquartzites because of the scarcity of data on other sandstones and the difficulty of computing the contribution of the rare placer sands known to be high in thorium (see MURRAY and ADAMS, 1958). Furthermore, the Zr/Th ratios in Table 11 strongly indicate that the Zr/Th ratio of 120 for sandstone is impossibly high because all the other Zr/Th ratios indicate very little fractionation of Zr/Th in the sedimentary processes, and this lack of fractionation is to be expected on the basis of their similarity in ionic radius and valence. Thus, either DEGENHARDT'S zirconium value for sandstone is too high, or—which is more likely—the thorium value for average sandstone is much too low. At the present time, considering the difficulties in assigning an accurate statistical weight to placer sands of high thorium content, it is interesting to consider what theoretical calculations can be made for the average thorium content of sandstones. Assuming that all the thorium values except that for sandstone are correct, one can calculate (as ADAMS and WEAVER, 1958, did) that the average sandstone contains 24 ± 7 p.p.m., thorium, which would give a low Zr/Th ratio of about 9. This last calculation represents a maximum value because it minimizes the weight of shales by taking the measured proportions of shale, sandstone, and carbonate rocks as 46 per cent, 32 per cent, and 22 per cent respectively. Taking the geochemical proportions used in Table 11, one would calculate 14 p.p.m. thorium, giving a slightly too high Zr/Th ratio of 16. If one assumes that DEGENHARDT'S balance for zirconium is essentially correct, and thus that the Zr/Th ratio in sandstones must be close to 13, one calculates a thorium content of about 17 p.p.m. A major difficulty in accepting such high average thorium values for sandstones is the qualitative experience that highly radioactive sandstones are apparently very limited in extent on the earth's surface and apparently unknown or unrecognized in the subsurface (see Fig. 1 and above discussion on sandstones). Only more data can finally resolve the several difficulties indicated in the balances presented in Table 11.

Several interesting aspects of the geochemical balance of uranium are suggested by the data in Table 12, where the readily soluble uranium in limestone (about

Table 12. Calcium and Uranium Concentrations in Limestones and Hydrosphere

	Limestones	Sea-water	River water
Calcium p.p.m.	400,000	400	30
Uranium p.p.m.	1·8	0·002	0·0001–0·001
Ca/U	220,000	200,000	30,000–300,000

80 per cent of the total; see discussion on carbonate rocks above) is compared with the total weight of calcium as the metal in pure calcite, giving a Ca/U ratio of 220,000. It is interesting to note how close this ratio in limestones is to the Ca/U ratio of about 200,000 in modern sea-water. The average concentration of uranium in solution in river waters can only be estimated to an order of magnitude (0·0001–0·001 p.p.m.; see Table 7) and both limits are used in Table 12, giving a Ca/U ratio of between 30,000 and 300,000.

The uranium value for limestones in Table 12 represents almost exclusively

rocks precipitated since the beginning of Cambrian time; if one assumes that the average Ca/U ratio in sea-water has not changed markedly from the modern value of about 200,000, it follows that the average Ca/U ratio in river waters during that time cannot be above 200,000, because a higher ratio would require the selective removal of calcium with respect to uranium, which is not observed. High Ca/U ratio rocks like anhydrite are so rare relative to limestone that it is more reasonable to require a maximum Ca/U ratio of about 200,000 in river waters, which in turn would call for a minimum uranium concentration of about 0·00015 p.p.m. in river waters. If this minimum concentration in river waters prevailed, there would be a simple steady state situation with a Ca/U ratio of about 200,000 in the average limestone, sea-water, and river water. However, this minimum concentration of 0·00015 p.p.m. uranium in solution in river water would only be enough to account for the uranium in limestones, leaving none to be removed from solution by fixation in other sediments like black shales and sapropelic deposits. Thus, the above line of argument suggests that the average concentration of uranium in solution in river water must be above 0·00015 p.p.m. Furthermore, the above argument indicates that the rôle of sapropelic, low *Eh*, sediments in the fixation of uranium from solution may have been overemphasized, because a minimum of 15 per cent of the uranium in sea water is accounted for by limestone alone if one assumes a maximum concentration of 0·001 p.p.m. in river waters and a constant Ca/U ratio in sea-water.

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The Separation of Thorium and Uranium in Sedimentary Processes

In all of the previous reviews mentioned in the introduction emphasis has been placed on the separation of thorium and uranium by processes in which primary igneous rocks are oxidized and leached during weathering and erosion. Under such conditions the uranium may be oxidized to the very soluble uranyl form and carried away in ground and surface waters. Thorium, on the other hand, cannot be oxidized under geologic conditions to a hexavalent state to form an analogue of the uranyl ion. Generally, any thorium brought into solution is quickly adsorbed or precipitated as an hydrolysate because of the unusually high ionic potential of the tetravalent thorium ion. This fundamental effect of weathering is partly responsible for the wide dispersal of thorium and uranium, and it also gives rise to the very low Th/U ratio observed in natural waters (see Table 9). However, not all of the uranium in igneous rocks is oxidized and leached during weathering. Some of the uranium, together with some of the thorium, remains in chemically resistant minerals such as zircon, monazite, and quartz. Thus, the partial separation of thorium and uranium during weathering and erosion can be considered as the result of the three major processes diagrammed in Fig. 4. Process *A* represents the removal of material in solution. Uranium, as uranyl ion, is so dissolved and removed, accompanied by considerably less thorium (see Tables 9 and 10). Process *B* represents the temporary solution of material, followed by its fixation in or on clay minerals and other secondary hydrolysates. Essentially all of the thorium brought into solution may be included in this material, and except for incomplete oxidation or very arid conditions, very little uranium is known to be in this material. Process *C* represents the mechanical transport of resistate minerals such as zircon, monazite, and quartz, which were formed under igneous conditions but have sufficient

mechanical and chemical stability to maintain their identity in sediments. These minerals carry with them whatever thorium and uranium they originally possessed.

The relative amounts of thorium and uranium affected by each of the three processes in Fig. 4 determine the distribution of these elements in sedimentary rocks. In turn these relative amounts depend upon the original sites of the thorium and uranium in the primary igneous rocks. Neuerberg's classification of these sites in igneous rocks has been discussed on p. 316, but for the present discussion these several sites can be divided into two groups: namely, the non-resistate group (processes *A* and *B*), and the resistate group (process *C*). The evidence regarding the relative amount of thorium and uranium in each

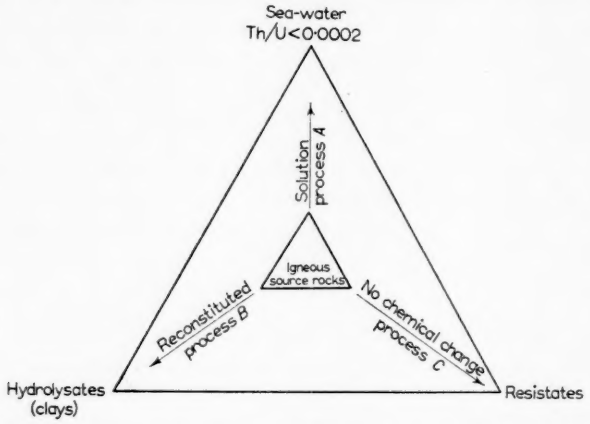

Fig. 4. The fractionation of uranium and thorium during weathering and erosion.

of these sites is based on three types of data: (1) leaching studies; (2) autoradiographic and petrographic studies; and (3) geochemical balances and interpretation.

Studies on the acid leaching of uranium, thorium, and unspecified radioactive material from igneous rocks, particularly granites, have been carried out by many workers (see p. 316), and it is evident that it is not uncommon for 15 to 40 per cent of the uranium in a granite to be leachable with 1M nitric acid (BROWN and SILVER (1956)). Although quantitative data such as those of BROWN and SILVER (1956) are available on only a few rocks, it is unlikely that more than 40 per cent of the uranium in average primary igneous rock is oxidized, leached, and transported to the sea (process *A* in Fig. 4). Indeed, assuming equivalence as regards grain size effects, leaching with anything as strong as 1M nitric acid must be considered more effective in dissolving uranium than normal weathering processes. One reason for this conclusion is that BROWN and SILVER (1956) found that apatite, which is uncommonly high in uranium (see Table 5) was brought into solution in their experiments, yet apatite, as a heavy mineral, certainly can retain its identity and its contained uranium in many sedimentary rocks. Another mineral that may be dissolved in leaching experiments is allanite, which is probably more important than apatite as a carrier of thorium and uranium (see p. 313). Assuming that allanite is as resistant

as the closely related epidote (see PETTIJOHN, 1957; and RANKAMA and SAHAMA, 1950, on the relative stabilities of minerals during weathering), it might be expected that allanite also persists to some extent in sediments. The rarity and the fine grain-size of allanite would make its recognition in sediments difficult.

Siliceous tuffs, because of their high surface-to-mass ratio, high uranium content, and the localization of some uranium in glass, can supply large amounts of uranium to ground water (DENSON *et al.*, 1956). The uranium leached from igneous rocks is in turn leachable from the sedimentary rocks in which it is deposited. This cumulative effect in the recycling of sediments is shown by the data of KOCZY *et al.* (1957), who found the uranium content of rivers draining sedimentary areas higher than that in rivers draining igneous areas.

Numerous autoradiographic and petrographic studies of primary igneous rocks, particularly granites, indicate that thorium and uranium are largely concentrated in accessory minerals (see p. 313), and it is likely that as much as 90 per cent of these elements on the average are to be found in minor minerals constituting less than 1 per cent by weight of the total rock. Many of these accessory minerals are highly resistant to weathering and are found intact, only slightly abraded, in sediments. Zircon, monazite, and xenotime are important carriers of thorium and uranium that belong to this highly resistant group. Somewhat less resistant carriers of thorium and uranium (such as apatite and perhaps allanite) may accompany the highly resistant minerals in favourable cases. Unfortunately for the present discussion, petrographic examination of the pertinent resistate minerals in sediments has been more concerned with the relative rather than the absolute concentration of these minerals, mainly because the finer size fractions of these minerals are so difficult to work with by conventional means. The same difficulty with fine grain sizes is encountered in attempting to localize thorium and uranium in clay and other hydrolysate minerals. The data on two bauxites (see p. 326) indicate that even in these products of extreme weathering, 90 per cent or more of the thorium and uranium are contained in resistate minerals like zircon and monazite.

The geochemical balances in Table 11 can be used to calculate some limits for the relative importance of the three processes shown in Fig. 4, Thus, assuming, as was done in Table 12, that about 80 per cent or 1·8 p.p.m. of the uranium in the average carbonate rock has been in solution in sea-water, one calculates that at least 7 per cent of the uranium originally present in the igneous source rocks has been transported in solution (process *A*). The uranium in marine black shales and phosphate rocks would raise this percentage. The low Th/U ratio in limestones is additional evidence to that cited above that very little thorium is transported by process *A*. The thorium and uranium in the orthoquartzites represent absolute minima for the amounts contained in resistates (process *B*), but for each element this represents only a few per cent of the total originally present in the igneous source rocks. The placer sands are undoubtedly sufficient to raise these minima somewhat. However, the shale term, including about 90 per cent of the thorium and uranium in sediments, is dominant.

Resistate minerals must carry some of the thorium and uranium found in shales, but it is difficult to estimate how much is carried in or on hydrolysate minerals, including clays. The slight, if any difference in the Zr/Th and Zr/U ratios in the igneous source rocks and in the average shale (Table 11) indicate that thorium, uranium, and zirconium are not markedly fractionated from

each other in the resistate mineral suite and/or in the secondary hydrolysate minerals. Considering the equal and constant valence and the similar ionic radii of thorium and zirconium, this constancy of the Zr/Th ratio is to be expected. However, the small fractionation of zirconium and uranium, as evidenced by the Zr/U ratios, is most readily explained by placing the zirconium and most of the uranium in resistate minerals in which the uranium is protected from oxidation, leaching, and separation from the zirconium. Furthermore, the small range in the uranium and Th/U ratios in shales suggests that the uranium and thorium in most shales is to be found largely in fine-grained, well-mixed resistate mineral suites that represent a fairly good sampling of the crustal thorium and uranium. If most of the uranium and thorium were held in or on secondary hydrolysate minerals, differences in sedimentary environments might be expected to cause much wider ranges in thorium, uranium, and Th/U ratios than those observed. It should be noted that zircon is the only major resistate carrier of uranium that also has a low Th/U ratio (see Table 5), and thus it must play a major rôle if the entire resistate, heavy mineral suite in shales is to dominate the thorium and uranium concentrations found.

All of the evidence just presented is consistent with an estimate that 60 to 85 per cent of the thorium and uranium in the igneous source rocks is contained in resistates that are carried over intact into the sediments (process *C*). Of the remainder, most of the uranium is transported to the sea in solution (process *A*), although some of it may be weakly held by adsorption on clays and other secondary hydrolysates (process *B*). Most of the thorium brought temporarily into solution is thought to be transported in or on secondary hydrolysates. Further studies, particularly of the sites of thorium and uranium in common shales, should reduce the range of the estimates.

The thorium and uranium mobilized and transported by means of the three processes described above and shown in Fig. 4 are deposited in the sediments by a variety of mechanisms. A significant fraction of the uranium in solution in sea-water is removed into limestones, and because other calcium precipitates (e.g. anhydrite) contain considerably lower concentrations of uranium than do limestones, some of the well-known carbonate–uranyl complexes in solution or on the carbonate solid phase have been hypothesized as the mechanism of fixation (ADAMS and WEAVER, 1958). Uranium is also extracted from sea water and fixed in the apatite of phosphate rocks, but the absolute amount of uranium so fixed is much smaller than that found in the much more abundant limestones. ALTSCHULER *et al.* (1956) have shown that some of the uranium in such sedimentary apatite is tetravalent, and phosphate–tetravalent uranium complexes favouring the formation of tetravalent uranium (BAES, 1956) may play a part in this fixation of uranium. An important fraction of the uranium in solution in natural waters is extracted by sediments rich in carbonaceous matter, e.g. lignite, coal, and marine black shales. Sediments of this type have been intensely investigated, and a number of mechanisms of fixation have been proposed. BREGER and DEUL (1956) have recently reviewed the evidence for these various mechanisms, and reduction by carbonaceous material or sulphide ion followed by adsorption or precipitation of the resultant tetravalent uranium form a class of very likely mechanisms. The direct precipitation of uranyl ion by carbonaceous material to form uranyl huminate has also been found to be operative. The limiting factor with such mechanisms is not their capacity to

remove uranium but the supply of uranium. Several workers (WEAVER, 1942; and ADAMS and WEAVER, 1958) have reported an inverse relationship between the rate of deposition and the uranium content of the sediment.

Although the evidence indicates that the transportation of thorium in solution is a very minor process, note must be taken of the deep-sea manganese nodules, which may contain as much as 124 p.p.m. thorium (GOLDBERG and PICCIOTTO, 1955). If the thorium in these nodules has been extracted from sea-water with a concentration of less than 2×10^{-5} p.p.m. Th (see Table 9), then these nodules are enriched in thorium by a factor of more than 10^6 over sea-water. However, the Mn/Th ratio in these nodules is many times greater than it is in the igneous source rocks, and the thorium in the nodules cannot account for the lack of thorium in the geochemical balance (Table 11). The possibility that aeolian transport of thorium in fine dust particles contributes to the thorium in these nodules cannot be neglected, because weathering concentrates thorium at the land surfaces, and the radioactive material in the atmosphere (see p. 333) indicates that thorium and thorium daughters may be more concentrated than uranium in fine dust particles and on the surfaces of particles in the soil.

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The quantitative importance of clay minerals and fine-grained hydroxides in the geochemical cycles of thorium and uranium is difficult to assess. It might be assumed that the proportion of thorium transported and deposited in these sedimentary materials equals the proportion of uranium transported in solution (15–40 per cent), but there is no empirical evidence from bauxites or other sediments that confirms that thorium has been temporarily in solution. On the other hand, the chemical evidence regarding the solubility of thorium as ions or in complexes leads to the conclusion that a significant fraction of the thorium transported must either be adsorbed on clay size material or precipitated.

A considerable fraction, perhaps more than two-thirds, of the thorium and uranium from igneous source rocks is thought to be transported in resistate minerals such as zircon, monazite, etc. The leaching experiments, the auto-radiographic and petrographic studies, and the interpretation of the geochemical balances discussed above all support this conclusion. It would follow that, by weight, these resistates are largely of silt and sub-silt size so that they are deposited mainly in the shales. The small grain size of these resistates is indicated by auto-radiographic studies and the observation of the centres of pleochroic haloes. Further reduction in grain size would be caused by abrasion during transport. A well-mixed, homogeneous suite of fine-grained resistate minerals in common shales would explain the strong similarities observed in the thorium, uranium, and zirconium contents of common shales as compared with the average igneous source rocks.

The above mechanisms for the separation of thorium and uranium in sedimentary processes are qualitatively well understood, whereas strictly plutonic mechanisms for the separation of thorium and uranium in igneous rocks are obscure and difficult to determine (see p. 319). One may hypothesize that the wide range of Th/U ratios observed in igneous rocks and veins may be due in part at least to the material having been sedimentary at some earlier time.

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GEOCHEMISTRY IN THE U.S.S.R. (1954-1956)

By S. I. Tomkeieff

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INTRODUCTION

In my previous review of the progress of geochemistry in the U.S.S.R. published in the *Physics and Chemistry of the Earth*, Volume 1, I covered the six years (1948–1953) and produced a bibliography of some 700 items. In the present review I am dealing with progress made during three years only but there are references to more than 1200 titles. The increase is due in part to a more extensive coverage of the field of publication, in a small part as well to the inclusion of a restricted number of works published prior to 1954, but still more to the remarkable increase in the amount of work done in this field. As in the previous review, however, only highlights are mentioned, and in the present case considerations of space have precluded detailed discussion of any subject. Often the text represents an annotated bibliography, summarizing the literature on any one selected topic. The term "geochemistry" has been interpreted very liberally to include all the fringes of this science, trespassing into the fields of chemical and structural mineralogy, petrology, the sciences of ore deposits, pedology, volcanology, oceanography, limnology, and even cosmochemistry as represented by the meteorites. In spite of its twelve hundred odd references this article covers geochemistry as developed in the U.S.S.R. through the medium of the principal publications only. Many periodicals, especially those published in the federal republics, are unavailable in England, and many books are unobtainable. In spite of these difficulties, i.e. incomplete record and compression in presentation, it is hoped that this review will be of use to workers in geochemistry and related fields and that it will in some measure surmount the barrier of language and bring the scientific workers of the east into closer contact with the scientific workers of the west.

Some of the works mentioned in this review have been abstracted in *Mineralogical Abstracts* and in *Chemical Abstracts* or other abstracting journals. Nearly all the translations of the Russian titles of books and articles are by the present author and some of them must appear strange to an English reader.

This is because certain Russian terms cannot be rendered accurately in English. Thus the term *zakonomernost* which can be accurately translated in German as *Gesetzmässigkeit* can only be translated in English very approximately as *regularity*.

Following the pattern of the previous review the present one is divided into six sections.

I. GEOCHEMISTRY, GEOSPHERES, ELEMENTS

1. *General*

The period under consideration is characterized by a remarkable increase in the number of publications. At the beginning of 1956 a new journal *Geokhimia* began to be published by the Academy of Sciences, and in the same year a new series entitled *Transactions of the Institute of the Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry* was inaugurated. Among semi-periodical substantial volumes one should note the following publications: *Types of dolomite rocks and their genesis, Crust of Weathering, 2, Problems of mineralogy of sedimentary formations* and the *Transactions of the 1st Congress of Thermography*. A new abstracting journal *Referativny Zhurnal* made its appearance in the middle of 1952 with its geological section making its appearance in the middle of 1954. This journal has not only a very extensive coverage but also some very extensive abstracts often illustrated by maps and diagrams. About two thirds of the total, averaging about 6000 abstracts per annum, is devoted to mineralogy, petrology, geochemistry and the science of ore deposits.

The Academy of Sciences has also undertaken the publication of collected works of V. I. Vernadsky, A. E. Fersman, E. S. Fedorov, F. Y. Loewinson-Lessing, A. N. Zavaritzky and D. S. Belyankin. Works on the history of science are very frequently published, and a few of them belonging to the subjects under review are by RESVOY (1953) RASKIN and SHAFRANOVSKY (1953), BUBLEINIKOV (1956), LAZARENKO (1954), LAZARENKO and KOROBTZOVA (1953), SLIVKO (1956) and PERELMAN (1956a). A general review of the development of geochemistry at home and abroad are given by V. V. SHCHERBINA (1954) and A. P. VINOGRADOV (1955a). A third and much enlarged edition of a popular book on geochemistry by FERSMAN has been published in 1954. Other popular books on geochemistry are those by PERELMAN (1955, 1956a) who develops the idea of "geochemical landscape" a concept introduced by the late B. B. Polynov, which expresses a rather complex relation existing between the natural features of a country and the prevailing geochemical factors in operation. A posthumous paper by the late P. N. CHIRVINSKY (1956) deals with the similarity in composition between meteorites and the mantle of the earth. A further development of the Lebedev-Belov hypothesis of the geochemical accumulators of energy is made by V. I. LEBEDEV (1954, 1956), while a criticism of this hypothesis is made by D. S. KORZHINSKY (1955). Another hypothesis relating to the internal structure and composition of the earth is developed by A. F. KAPUSTINSKY (1956a, b, c) according to whom the central part of the earth, the "cenrisphere" is composed of "metallized" atoms of the light elements, stripped of their outer electrons and thus in a "degenerate" state in which the real difference in the chemical properties of the elements is completely lost and chemical reactions are impossible. The origin of the earth's crust is discussed by EIGENSON (1956).

The following sundry geochemical problems are discussed: calculation of

specific gravity of simple substances, effective ionic radii and strength of bonds in minerals by Povarennykh (1955, 1956a, b), the velocity of migration of water by MAXIMOVICH (1954), joint migration of solids and liquids, by OLSHANSKY (1956) and on the classification of natural gases and on the ratio of inert gases to nitrogen in natural gases by C. P. FLORENSKY (1956a, b).

2. *Elements and their Distribution*

Various aspects relating to the distribution of the elements are discussed by VINOGRADOV (1956a), LEBEDEV (1955) and CHERDYNTZEV (1956). The problems of migration of elements are discussed by BURKSER *et al.* (1954), SHCHERBINA (1953, 1956a, b, c) and OVCHINNIKOV (1956). The influence of pressure on the periodic properties of the elements is discussed by RYABYNIN (1955), and the periodic function of the ratio of the heat of fusion to the temperature of fusion is discussed by BOCHVAR and KUZNETZOV (1954).

The geochemistry of the following elements is dealt with: beryllium by BEUS (1956a, b), BEUS and FEDORCHUK (1955), BEUS and SAZHINA (1956), BORODIN (1956); cobalt, by UNKSOV (1954), MALYUGA and MAKAROVA (1954); nickel, cobalt, and copper by RONOV *et al.* (1955), tin by BARSUKOV and PAVLENKO (1956); lead by ZHIROV and ZYKOV (1956); lead and zinc by TAUSON and PEVTZOVA (1955), TAUSON and KRAVCHENKO (1956), GINZBURG and MUKANOV (1956); zinc by ZAGYANSKY (1954); tantalum by GINZBURG (1956); titanium by DMITRIEV and ZNAMENSKY (1956), OSTROUMOV (1956a, b, c); manganese by OSTROUMOV (1955); phosphorus by ZARITZKY (1956); scandium by BURKSER *et al.* (1955); hafnium and zirconium by TUGARINOV *et al.* (1956); niobium by BORODIN (1955); uranium by TAUSON (1956), TAUSON *et al.* (1956); thorium and uranium by BARANOV *et al.* (1956); rare earths by VAINSTEIN (1956), VAINSTEIN *et al.* (1955, 1956); iodine by RONOV *et al.* (1955), ITKINA (1956), SAVCHENKO (1956); iodine and bromine by ITKINA (1955); bromine by VALYASHKO (1956); silver and gold by SHCHERBINA (1956); various elements by TAUSON (1954), BRUEVICH (1955), STRAKHOV *et al.* (1956), LAVROV (1956), KATCHENKOV (1955, 1956).

3. *Radioactive Elements and the Age of the Earth*

Unfortunately only a small part of the published material on this subject was available, and it was therefore felt that any attempt to give a consistent account of the progress made in this branch of science would be highly misleading. It was decided, therefore, to give only the list of references in the alphabetical order of the names of the authors:

AFANASIEV (1955), AMIRKHANOV and BRANDT (1956), AMIRKHANOV *et al.* (1955), BARANOV (1956), BARANOV and KUZMINA (1954), BOROVIK-ROMANOVA and ZMEENKOVA (1956), GERLING (1955, 1956b), GERLING *et al.* (1956), GERLING and PEKARSKAYA (1954), KOMAROV (1956) (in this work the age of certain rocks is determined by a palaeomagnetic method), KOMLEV *et al.* (1956), KOMLEV *et al.* (1956), POLEVAYA (1956), POLEVAYA *et al.* (1955), STARIK (1956), STARIK *et al.* (1955), STARIK *et al.* (1956), TOKAREV and SHCHERBAKOV (1956), TUGARINOV (1954), TUGARINOV and ZYKOV (1956), VINOGRADOV (1956b), VINOGRADOV *et al.* (1956), VINOGRADOV *et al.* (1956), VINOGRADOV *et al.* (1956), VINOGRADOV *et al.* (1954), VOITKEVICH (1954, 1955a, 1956), ZADOROZHNY and BYKOVSKY (1956), ZHIROV and ZYKOV (1956a), ZYKOV and STUPNIKOVA (1956).

4. *Isotopes*

In a brief article VINOGRADOV (1954) discussed the geochemistry of the isotopes, pointing out that their relative abundance is linked up with their atomic structure.

(a) Oxygen—PEREDERIEV (1955) found that in comparison with the oxygen of the river water, used as a standard, the maximum content of 0^{18} in pyrolusite is 3·6γ, in manganite 2·8γ and in psilomelane 3·3γ and that in general the amount of 0^{18} increases with the increase of the amount of the four-valent manganese in the mineral. DONTZOVA (1954, 1955a, b, 1956) made a detailed study of the exchanges of the oxygen isotopes between the natural SiO_2 and CO_2, between the minerals belonging to the oxides group and CO_2 between the atmosphere and the lithosphere. She also studied the mobility of oxygen in silicates and aluminosilicates. TROFIMOV (1954a, b) studied the exchange of the oxygen isotopes between carbonates, O_2 and CO_2. TEIS (1954, 1955) studied the oxygen isotopic composition of waters of crystallization and in natural sulphates. NAIDIN *et al.* (1956) in their application of oxygen isotopes palaeothermometry methods to belemnites of the Upper Cretaceous age in Russia found palaeotemperatures of the seas ranging from 13·3° to 23·8°C.

(b) Sulphur—VINOGRADOV *et al.* (1956) by assuming as standard ratio S^{32}/S^{34} that of troilite from Sikhote Alin meteorite, equal 22·02, found in pyrites of various ages, this ratio varied from 21·280 to 23·261, and in sulphates—from 21·520 to 21·838. Statistical evidence precluded the authors of assuming the possibility of relating the isotopic composition to the age of minerals. In a later publication VINOGRADOV, CHUPAKHIN and GRINENKO (1956) found that a higher ratio was observed in the case of low temperature and metacolloidal pyrite and marcasite—all products of biogenic reduction, and that a higher ratio was observed in sulphides of magmatic, hydrothermal and contact-metasomatic origin.

(c) Lead—the isotopes of lead are discussed by VINOGRADOV (1955), VINOGRADOV and ZYKOV (1955), VOITKEVICH (1955), STARIK and SOBOTOVICH (1956), RABINOVICH *et al.* (1956) and TUGARINOV (1955).

(d) Uranium—PETRZHAK *et al.* (1956), from the study of the isotopic composition of uranium in meteorites, concluded that the isotopic composition of uranium in meteorites and in the earth is practically the same.

(e) Carbon—A brief instruction on isotopic analysis of carbon is provided by GOLUBCHINA (1956).

5. *Meteorites*

A new book on meteorites is published by KRINOV (1955) and a new classification of meteorites is proposed by YAVNEL (1956). The latter is a modification of the existing classification and combines the chemical and the mineralogical aspects of meteorites. The iron meteorites are divided into five groups according to the percentage of nickel in the metal. This figure, combined with the percentage of metal itself, provides a basic framework for the classification of all meteorites, which are ranged from achondrites to siderites and subdivided into six sub-classes, each of them in turn divided into groups according to the percentage of nickel, and then in types according to their mineral composition and, finally, into sub-types according to their structure. YAVNEL (1954) also published the results of spectroscopic analysis of a large number of meteorites.

STARIK and SHATZ (1956) provide the results of determination of uranium in meteorites by the luminescence method, with a variation from $0{\cdot}8 \times 10^{-8}$ g/g to $2{\cdot}4 \times 10^{-7}$ g/g. RIK and SHUKOLYNKOV (1954) provide data for the isotopic composition of potassium in meteorites, with the ratio K^{39}/K^{40} averaging 14·4 in eucrites and 14·3 in chondrites. STARKOVA (1955) gives the results of determination of uranium and thorium in fifty siderites and a number of siderolites and stony meteorites. GERLING and RIK (1954, 1955) provide new determinations of the age of stony meteorites, varying from 640 to 4500 million years. YUDIN (1954, 1956) provides data on the mineralogical and chemical composition of meteorite Vengerovo. Also he describes the following minerals found in meteorites—ilmenite, iozite, native copper and magnetite. GERLING (1956) studied the inert gases extracted from meteorites at 1150°C. In all cases he observed a high content of A^{40} and a ratio A^{36}/A^{38} different from that found in the air, while the proportions of $Ne^{20}:Ne^{21}b:Ne^{22}$ are shown to be close to unity. GERLING and LEVSKY (1956) in discussing these results find that they support the hypothesis that meteorites are the products of disintegration of a cosmic body of planetary dimensions. CHERDYNTZEV and ABDULGAFAROV (1956) provide data for the content of helium in four stony meteorites, ranging from $0{\cdot}5 \times 10^{-5}$ to $3{\cdot}6 \times 10^{-3}$ cm^3/g. KRINOV and FONTON describe the meteoritic dust of the Sikhote-Alin meteorite shower.

6. *Crystals and Crystal Structure*

(a) Crystal morphology, or the external aspect of crystals and their physical properties, are at the present time so closely linked up with their fine structure and their genesis that a study of these aspects is becoming an integral part of geochemistry. The works in this field are only briefly outlined in the present section. Thus V. D. KUZNETZOV (1954) has produced a large and comprehensive treatise on crystals and crystallization, which includes the following topics: nucleation, crystal kynetics, devitrification, growth and solution of crystals, etch figures and solution forms, mosaic crystals, surface energy, allotropy, polymorphism and isomorphism. Geometrical crystallography as related to crystal chemistry, is discussed by SHUBNIKOV (1954a, b, 1955a, b), MIKHEEV (1954, 1955), MIKHEEV and SHAFRANOVSKY (1955), KAZITZIN and ALEXANDROV (1956), SHAFRANOVSKY (1954). Growth and solutions of crystals are discussed by GRDINA and ELISEEVA (1956) LEMMLEIN (1954), VAZBUTZKY (1954), STULOV (1954), KRIZHTAL (1954), GASILOVA *et al.* (1953). The surface features of crystals, by LEMMLEIN and GLIKI (1954), SHAFRANOVSKY and MOKIEVSKY (1952, 1956), SEELIGER (1956), KORNILOV (1954), SHAFRANOVSKY (1953), GENKIN (1954), GRIGORIEV (1956) KARYAKIN and KAINARSKY (1953).

(b) Inclusions in crystals and gaseous, liquid and solid inclusions in crystals, temperatures of homogenization, geological thermometry, methods and apparatus—are discussed by: DOLGOV and RAIKHER (1953), KALYUZHNY (1954, 1955a, b, 1956), LEMMLEIN (1956), LEMMLEIN and KLIYA (1954), LEMMLEIN and KLEVTZOV (1956a, b), LOSKUTOV (1955), NIKOLAEVA (1954), PIOTROVSKY (1953), SUKHORSKY (1953), VULCHIN (1952), KALYUZHNY and KOLTUN (1953).

(c) Crystal structure—SOBOLEV (1956) discusses the properties of silicates as determined by their fine structure. BELOV (1950–1956) in a series of articles discusses in detail the fine structure of a large number of minerals and compounds together with certain problems of crystal chemistry. VAINSTEIN (1952)

provides a mathematical method of deciphering of crystal structures by a set of complex numbers. PINSKER (1952) applied electronographic methods to the analysis of BiI_3 and discusses the structure of substances processing layer structure. BEUS (1956) provides a detailed study of the geochemistry of beryllium and discusses the isomorphous entry of beryllium into the crystalline lattice of minerals.

The following minerals were studied from the structural standpoint: apatite, by OZEROV *et al.* (1956), chkalovite, by PYATENKO *et al.* (1956), cuspidine, by SMIRNOVA *et al.* (1955), eremeyevite, by GOLOVASTIKOV *et al.* (1955a, b), garnet by GNEVUSHEV *et al.* (1956), organic minerals, by GILLER (1955), wollastonite, by MAMEDOV and BELOV (1956), xonotlite, by MAMEDOV and BELOV (1955, 1956), zoisite, by FESENKO *et al.* (1955).

GORYUNOVA *et al.* (1955) have studied the isomorphism of certain compounds of Ga and Zn, MIKHEEV (1955a) proposed a formula for the calculation of cell dimension of spinels and TOBELKO *et al.* (1954) have provided data for the structure of realgar and on the atomic radius of As.

7. *Methods*

(a) Luminescence—BARSANOV and KRUGLOVA (1954), BARSANOV and SHEVELEVA (1954, 1955), GRUM-GRZHIMAILO *et al.* (1955), KOMOVSKY and LOZHNIKOVA (1954), KONSTANTINOVA-SHLEZINGER (1954), LEONOVA (1956), STARIK, ATRASHENOK and KRYLOV (1956b).

(b) Spectroscopy—BOROVIK-ROMANOVA (1956), INDICHENKO (1955), RUDNITZKAYA (1956), SHAILIKOV (1954), VEDENEEVA (1956), GRUM-GRZHIMAILO *et al.* (1952).

(c) Varius—BARANOV and TLEUBERGENOVA (1956), CHIRVINSKY (1955), GETZEVA and SAVELIEVA (1956), GRITZAENKO (1956), GURVICH and KHANAEV (1956), IVANOV (1954), IVANOVA and KHRISTIANOV (1956), KANYUKOVA (1956), LOGVINENKO and ZABOLOTNAYA (1954), NOVIKOV and BUKHANOVA (1956) PALVELEV and ANDREICHEVA (1956), PCHELINTZEV (1956), STARIK, ATRASHENOK and KRYLOV (1956a).

INTRODUCTION AND SECTION I—REFERENCES

All references unless indicated are in Russian

Abbreviations:

BUL	*Bull. Volcan. Station, Acad. Sci. U.S.S.R.*
DOK	*C.R. (Doklady) Acad. Sci. U.S.S.R.*
DOL	Types of dolomite rocks and their genesis, *Trans. Geol. Inst.*
GEO	*Geochemistry (Geokhimia)*, Publ. Acad. Sci. U.S.S.R.
HAL	*Trans. All-Union Sci.-Prosp. Inst. Hallurgy.*
IZV	*Bull. (Izvestia) Acad. Sci. U.S.S.R., Sér. géol.*
MUS	*Trans. Mineralogical Museum Acad. Sci. U.S.S.R.*
SBO	*Mineralogichesky Sbornik Lvov Geol. Soc.*
SED	*Problems of mineralogy of sedimentary formations.* Publ. Univ. Lvov.
THE	*Trans. First Congr. Thermography, Acad. Sci., U.S.S.R.*, 1955.
TIG	*Trans. Inst. Geol. Ore Depos., Petr., Miner., Geochemistry, Acad. Sci. U.S.S.R.*
VOL	*Trans. Labor. Volcanology. Acad. Sci. U.S.S.R.*
WEA	*Crust of Weathering (Kora Vyvetrivaniya)*, Acad. Sci. U.S.S.R.
ZAP	*Mem. (Zapiski) All-Union Miner. Soc.*

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II. MINERALS

1. *General*

In 1956 the well known text-book of mineralogy by BETEKHTIN (1956) appeared in the second edition and a practical manual on mineralogy was published by SMOLYANINOV (1955). The concept "mineral" and the object of the science of mineralogy have been debated by POVARENNYKH (1954) and GRIGORIEV (1956b). The problem of classification of minerals has attracted a number of persons. Thus KOSTOV (1956) provides a scheme of classification of oxides based on physical and crystallochemical aspects, and in a separate article KOSTOV (1954) discusses wider aspects of classification. According to BOKY (1956) the classification of minerals, as well as all the chemical compounds, must be based on the periodic system of the chemical elements. Other aspects, such as the nature of the bond between atoms, structural types of crystalline structures, must also

be regarded as principles of classification. A consistent and full scheme of classification of minerals is developed by POVARENNYKH (1956d). This classification is based on chemical types and on structural types of minerals. Another generalized problem, that of connexion existing between various properties of minerals or rocks, and its evaluation by means of coefficient of correlation, is discussed by VISTELIUS (1956).

Among works dealing with group or types of minerals or mineral formations one may mention the work of SHCHERBINA (1954) on minerals of variable composition as indicators of the medium from which they were formed, GINZBURG (1956) on metamict minerals, KRUGLYAKOVA (1954) on magnetic susceptibility of minerals, GRUSHKIN (1954) on incrustations on minerals, POVARENNYKH (1956a) on the relation between the melting temperatures of minerals and their crystallochemical aspects. CHIRVINSKY (1953) provides a large number of averages of the chemical composition of the principal rock-forming minerals.

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Minerals of colloidal origin are discussed by various authors, such as BRODSKAYA and ZAKHAROVA (1956), SEDLETZKY (1954), SEDLETZKY and LARIONOV (1955), OREKHOV and SEDLETZKY (1954), GRIGORIEV (1956a), and CHUKHROV (1955b). A large and comprehensive volume on colloids and colloidal minerals in the earth's crust is published by CHUKHROV (1955a). This volume also contain chapters dealing with colloidal processes, colloidal formations and many other related subjects. In this book Chukhrov proposes a new mineral name—ginzburgite—for a group of clay minerals roughly corresponding to the formula $(Al, Fe)_2O_3 . 2SiO_2 . nH_2O$.

2. *Thermal Analysis*

A review of the progress and development of thermography in Russia, since the invention of the automatic registering pyrometer by N. S. KURNAKOV in 1904, is given by BERG (1955). KELER (1955) describes the apparatus and methods of complex analysis of silicates with an automatic record of thermal, loss of weight and dilation curves. MCHEDLOV-PETROSYAN (1955) discusses the exothermal effect in such layer silicates as kaolinite, antigorite and serpentine. TZVETKOV and VALYASHIKHINA (1956a, b) provide data for muscovite, hydromuscovite, phlogopite, sericite, paragonite, biotite, hydro-biotite, vermiculite, glauconite and lithium micas. KORZHINSKY (1955) and OVCHINNIKOV *et al.* (1955) provide detailed data for a number of amphiboles. SOBOLEV and TZVETKOV (1956) discuss the thermal curves of disthene and andalusite. TUMANOV and MASLENNIKOVA (1956) show the application of thermal analysis to the determination of the degree of kaolinization of spodumene. ALESHIN (1955) applies thermal methods to the study of the transformation of clay minerals in soils, while GORBUNOV and SHURYGINA (1955) apply these methods to the study of soils themselves. KAURKOVSKY (1955a, b) provides a study of siderite and in this outlines a new method of study of the genesis of certain iron ores. RODE (1955) provides a detailed combined thermal, chemical and X-ray study of various manganese oxides minerals, including manganosite, manganite, hausmannite, braunite. He also proposes a new mineral name, kurnakite, for the two modifications of Mn_2O_3. Other thermal studies include the work of ŽÁK (1956) on alabandite, BERG *et al.* (1955) on natural salts, including a generalized review of the recent Russian work on this subject, KUZNETZOVA (1955) on the carbonate and sulphate rocks associated with salt deposits,

KANAVETZ *et al.* (1955) on solid fuels, KLIMOV *et al.* (1955) on bituminous shales. Apparatus and methods of thermal analysis are discussed by KAURKOVSKY (1955c) TEILTELBAUM (1955), BERG *et al.* (1955), POTAPENKO (1953) and TZVETKOV *et al.* (1955).

3. *Experimental mineralogy and slags*

(a) Experimental mineralogy—Among recent books dealing with subject there is a book by BOTVINKIN (1955) in which the various silicates and silicate systems are discussed, and the furnaces and other apparatus are described. Then there is a new edition of the well known book on the physico-chemical system of silicate technology by BELYANKIN *et al.* (1954).

Problems of thermodynamics in mineral systems are discussed by NIKOLAEV (1952, 1954, 1955, 1956); mineral formation in certain silicate melts by OSTROVSKY (1956a, b); the rôle of pressure by SOBOLEV (1955); hydrothermal ore solutions by SYROMYATNIKOV (1955), RAFALSKY (1956) and OVCHINNIKOV and SHUR (1956); mineral formation in an electric field by MOKIEVSKY *et al.* (1956); application of electrodyalysis by IVANOV and SHEINA (1956): formation of metamict minerals by CHESNOKOV (1956) and POVARENNYKH (1956c).

The following systems or parts of systems are described: H_2O–SiO_2, by KHITAROV (1956), H_2O–CO_2, by KHITAROV and MALININ (1956); Cr–Cr_2O_3–CaO, by OLSHANSKY *et al.* (1956); LiCl–$CaWO_4$, by ANIKIN (1956); nepheline–kaliophylite–silica and orthoclase–albite–anorthite, by SOBOLEV (1956); fayalite–magnetite, by OSTROVSKY and OLSHANSKY (1956).

The following minerals were synthesized or experimentally studied: autunite, by SHCHERBINA and IGNATOVA (1956); ferrisilicates and ferrosilicates by SOKOLOVA *et al.* (1954); ferritungstite by KHRISTOFOROV (1955); K–Fe–hydroxyle mica, by VERES *et al.* (1955); merwinite by ALENTIEV and KOROVNICHENKO (1955); mullite by KARYAKIN and MARGULIS (1956); nasturan by NAUMOV and TOBELKO (1956); sodium sulphate, by KHLAPOVA (1955); spinels by LAPIN (1955); uranium binding by humic acids by MANSKAYA *et al.* (1956).

(b) Slags—A comprehensive treatise on the petrology and chemistry of slags and clinkers is published by LAPIN (1956b). It contains a large number of chemical analyses of slags and slag minerals and abundant optical and X-ray data and is provided with a bibliography of some 600 items. Other works on slags include those of LAPIN (1954, 1956a); LAPIN *et al.* (1956); KURTZEVA (1956); DOLKART and GULKO (1954).

4. *Native Elements*

Diamond is discussed by ANSHELES (1955); FUTERGENDLER (1956); GNEVUSHEV (1955, 1956a, b); MITROFANOVA (1955, 1956). Graphite is discussed by ONTOEV (1955); native tin by ALEXANDROV (1955).

5. *Sulphides, Arsenides, etc.*

Lead and zinc sulphides are discussed by RUDENKO (1954), KOLBIN and PIMBURGSKAYA (1955b), BLOKH (1954), KONSTANTINOV (1954), LEBEDEV (1954a, b), YASINSKAYA (1953, 1955), KUTINA (1956) and LAZARENKO (1955a). Pyrite and similar minerals are discussed by MALKHASYAN (1954), FRANTZKAYA (1956), GENKIN (1955), VEITZ (1952), and SHADLUN (1953). Other minerals: bertierite by GUKOVA (1954), bismuth sulphosalts by SAKHAROVA (1955); bis-

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mutite by NEFEDOV (1956a); chloanthite by BADALOV and PRIKHIDKO (1956); cosalite by ERMILOVA and SENDEROVA (1955); ferroselite a new mineral, by BURIANOVA and KOMKOV (1955) and BURIANOVA (1956); joseite by GRIGORIEV and DOLOMANOVA (1955a); pentlandite by ELISEEV (1955); tennantite-tetrahedrite group (fahlerz) by LAZARENKO (1956a); wolfsbergite by SHADLUN (1954); zinkenite by GORZHEVSKY (1955). Oxidability and magnetic susceptibility of sulphides and arsenides are discussed by YAKHONTOVA and RAUDONIS (1956) and KRUGLYAKOVA and YASINSKAYA (1952).

6. *Halides*

Fluorite is discussed by YAKSHIN (1954); FEOFILOV (1956) and KHODAK (1956); carnallite by KOROBTZOVA (1954) and halite and sylvine by KORENEVSKY (1954).

7. *Oxides*

Various aspects of quartz are discussed by BUTUZOV and IKORNIKOVA (1954, 1956); CHENTZOVA and VEDENEEVA (1952a, b), DIBROV (1955), FIRSOV (1955), GENKIN (1954), GINZBURG and VITOVSKAYA (1956b), GRIGORIEV (1954), GRIGORIEV and GAMSULOVA (1955), IKORNIKOVA and BUTUZOV (1955), KARAYAKIN (1954a), KRENIG and LAZKO (1952), LISITZINA (1956), MARTYNOVA (1955), NEMETZ (1954), PETRUN (1954, 1955), TZYGANOV (1953) and VERTUSHKOV (1954a).

Inclusions in quartz are studied by BUTUZOV and IKORNIKOVA (1955), DOLGOV (1955), KARAYAKIN (1954), LEMMLEIN and KLEVTZOV (1955), STRONSKAYA (1955), VULCHIN (1953) and YAKUBOVA (1955).

Tridymite is described by FISHKIN (1956); cristobalite by MENYAILOV (1955); chalcedony by BOGDANOVICH and DMITRIEVA (1956) and RUSKO (1953, 1954) and a new mineral, an aluminium alkaline opal, named bobkovite, is described by KAZITZYN (1955).

Iron oxides are studied by FRANK-KAMENETZKY (1954), PAVLOV (1956), POVARENNYKH (1952), TZYGANOV (1951), and YURK (1956); spinels by KARAYAKIN and PYATIKOP (1955a, b), SERDYUCHENKO and MOLEVA (1955) and SUMIN (1955b), brookite and anatase by KORNETOVA (1954b); magnetite by ERMAKOV and SHUR (1955) and by OVCHINNIKOV and SHUR (1955); rutile and ilmenite by ZIV (1956) and YAROSH (1955); sinhalite by SHABYNIN; cassiterite by KONSTANTINOV (1956); gahnite by BAZHENOVA (1955b); uranovanadate by MORACHEVSKY and BELYAEVA (1956); knopite, metaloparite and other minerals of the perovskite group by BORODIN (1954).

The new oxide minerals are: kurnakite, as given above in the section on thermal analysis; bobkovite, as mentioned above; irinite, a mineral belonging to the group of perovskite, described by BORODIN and KAZAKOVA (1954); zirconolite, a complex oxide of the AB_3O_7 type, described by BORODIN, NAZARENKO and RIKHTER (1956); hydronasturan and urhyte, hydrous oxides of uranium, described by GETZEVA (1956). Finally PADĚRA and FIŠERA (1956) have proved that arsenolamprite is not a distinct mineral but a mixture of arsenic and arsenolite (As_2O_3).

8. *Carbonates*

The following carbonates are described: artinite by SLAVSKAYA (1955); calcite by LEBEDEV and STEPANOV (1955) and SKROPYSHEV and MOKIEVSKY (1955); calcium rhodochrosite (manganocalcite) by STANKEVICH (1955); dolomite by

YASINSKAYA and KOLTUN (1956); magnesite by FROLOVA (1955). Other carbonates by GRYAZNOV (1955), KAZMINA (1954), KORMILITZIN (1955), KORZHINSKY (1956b) and SHCHERBINA and IGNATOVA (1955).

9. *Phosphates, Arsenates, etc.*

The following minerals are described: vivianite by KNYAZEVA (1954); destinizite by GERMAN (1956); newberrite, together with collophane, vivianite and pyrrhotine, from mammoth's tusks by VERTUSHKOV (1955a, b). ELISEEV (1954) proved that chinoite is identical with libethenite. MARTYANOV and PINEVICH (1954) discovered a new mineral belonging to the group of sicklerite. YAKHONTOVA (1956) discovered a new mineral, smolyaninovite, a variety of hydrous oxyarsenate. BORODIN and KAZAKOVA (1954a) described a new mineral and named it belovite, which was a variety of phosphates, but it was discovered that the name belovite was already given by NEFEDOV (1953) to a variety of arsenate. To solve this clash, YAKHONTOVA and SIDORENKO (1956) proposed two distinct names: arsenate-belovite and phosphate-belovite. According to SUMIN (1955) libethenite and olivenite form an isomorphous series. GINZBURG (1954) studied the process of oxidation of iron phosphates.

10. *Sulphates*

The following minerals are described: anhydrite by BADALOV (1954, 1955), alunite by SOBOLEV and FISHKIN (1953) and KARAYKIN and REMISOV (1956), barite by VARTERESEVICH (1953, 1956) and LAZARENKO (1955b) gypsum by ZOLOTUKHIN (1954), melanterite by SIDORENKO (1955), plumbojarosite by VAKHRUSHEV (1954). A new mineral belonging to the group of alums and named shorsuite, is described by VINNICHENKO (1955).

11. *Silicates*

BOKY and BATZANOV (1956) have proposed a new group of silicate minerals, called by them oxysilicates, to include those silicates in which oxygen does not enter fully into the silica framework, as in kyanite $Al_2[SiO_4]O$, ramsaite $Na_2Ti_2[SiO_3]O_3$. These considerations prompted these authors to construct a new table of classification of silicates, based on chemical and crystallochemical characters.

Works dealing with the silicate minerals are very numerous and exigencies of space in this article allows only a bare mention of authors' names dealing with a given mineral or topic:

Feldspars—BALASANYAN (1956), BAZHENOVA (1955a), BOBROVNIK (1952). FIRSOV (1956), KAZAKOV (1956), LEBEDINSKY (1955), RUDENKO (1954), SHUTOV (1956), SLIPCHENKO (1955), TATARSKY (1956), VERTUSHKOV (1954, 1956) VLASENKO (1954), and VLODAVETZ and SHAVROVA (1953).

Irization in feldspars—AGAFONOVA (1952, 1953, 1954, 1955, 1956), MIKHEEV and RUDENKO (1954), and PAZYUK (1954).

Zeolites, etc—BARABANOV (1955, 1956), BOBROVNIK (1953), ERMOLOVA (1955), GINZBURG and GUSHCHINA (1954), IVKIN (1955), KOLBIN and PIMBURGSKAYA (1955a), KORNETOVA (1954c), SUMIN (1955a), VASILIEV *et al.* (1956), and YANULOVA (1956).

Micas—BERKHIN (1954), BOBROVNIK (1954), EVSIKOVA (1954), GIRICH (1952), GRUM-GRZHIMAILO *et al.* (1955), KORNETOVA (1954a), MAKHININ

(1954), MIKHEEV (1954), MIKHEEV and STULOV (1955), MURAVIEV (1956), PARFENOVA (1956), POLOVINKINA and SHENDEROVA (1954), SERDYUCHENKO (1954b, c), SHUSTOV (1956), SUDOVIKOVA (1956), TZVETKOV and VALYASHIKHINA (1956), TZYGANOV (1954), YAMSIN *et al.* (1955) and ZVYAGIN (1954).

Amphiboles and Pyroxenes—BELEVTZEV *et al.* (1955), KORZHINSKY (1956a), LEBEDINSKY (1952), LITZAREV (1956), MELANKHOLIN (1956), POLOVINKINA (1953), SERDYUCHENKO (1954a), VERTUSHKOV and YAROSH (1956a, b), and ZHARIKOV and VLASOVA (1955). A new mineral belonging to the amphibole group, named istisuite, is described by KASHKAY and MAMEDOV (1955).

Garnets—GRUM-GRZHIMAILO *et al.* (1954), LAVRENKO and LAZKO (1954) SERDYUCHENKO (1955), SOBOLEV *et al.* (1955).

Tourmalines—ONTOEV (1956b), SHENDEROVA (1955), SLIVKO (1952, 1955) and TARNOVSKY (1954).

Chlorites—BERKHIN and SERDYUCHENKO (1953), GINZBURG and NIKITINA (1956), KUKOVSKY and SEDLETZKY (1956), LAZARENKO (1954), ONTOEV (1956a).

Glauconite—DYATCHENKO and KHATUNTZEVA (1956*c*), KUZNETZOV and SHEVYREV (1956), LAZARENKO (1956c), LAZARENKO and KUDRIN (1956), LOBANOV (1956), MAKHININ (1951), MIKEY (1956), SHAMRAY (1954) and ZAPOROZHTZEVA (1954).

Palagonite and Chlorophaeite—GONSHAKOVA (1956) SHASHKINA (1956).

The following minerals are arranged in an alphabetical order: axinite, SOLOVIEV (1956); beryl, BEUS and ZALASHKOVA (1956), GINZBURG (1955a); bertrandite, CHUKHROV and SMOLYANINOVA (1956), GRIGORIEV and DOLOMANOVA (1955); britholite, NECHEVA and BORNEMAN-STARYNKEVICH (1956); celadonite, KVALVASER (1953), LAZARENKO (1956b), MALKOVA (1956), SAVICH-ZABLOTZKY (1954); cerolite, SLANSKY (1955); cookeite, ZVYAGIN and NEFEDOV (1954); cuspidine, KARAYKIN and GULKO (1954); epidote and zoisite, KOSSOVSKAYA and SHUTOV (1956); hisingerite NIKOLSKY (1953); ilvaite, GORBUNOV and KORNILOV (1954), KHETCHIKOV (1956); lithionite, GINZBURG (1955c); orthite, VARTANOVA and ZOLOTUKHIN (1955); palygorskite, ZKHUS (1956); potash scapolites, SERDYUCHENKO (1955b); sauconite, GINZBURG and VITOVSKAYA (1956a), SEMENOV (1956a); sepiolite, RATEEV (1954), RATEEV and KOTELNIKOV (1956), MCHEDLOV-PETROSYAN (1954); serpentine, MCHEDLOV-PETROSYAN (1954); topaz, KARPENKO (1954); GRIGORIEV and DOLOMANOVA (1954b); viluite, LYAKHOVICH (1955); zircon, PREOBRAZHENSKY (1955), VARKHRUSHEV (1956).

The following new minerals are described: Beryllite $Be_3SiO_4.(OH)_2H_2O$, by KUZMENKO (1954). FERRIKEROLITE $Fe_2O_3.MgO.SiO_2.H_2O$, by RUKAVISHNIKOVA (1956). Ferroferrimargarite by GINZBURG (1955) (see BONSHTEDT-KUPLETSKAYA (1956)). Karpinskyite $Na_2(Be, Zn, Mg)Al_2Si_6O_{16}(OH)_2$ by SHILIN (1956). Karpinskite $(Ni, Mg)_4(OH)_4[Si_4O_{10}]$ by RUKAVISHNIKOVA (1956). Kupletskite $K_2Mn_4Ti\,[Si_4O_{14}](OH)_2$ by SEMENOV (1956b). Kurumsakite $8(Zn, Ni, Cu)4Al_2O_3.V_2O_5.5SiO_2$ by ANKINOVICH (1954). Labuntzovite, replacing the name titanoelpidite, (K, Na, Ba, Ca, Mn) (Ti, Nb) $Si_2(O, OH)_7.0{\cdot}6\,H_2O$ by SEMENOV and BUROVA (1955). Nenadkevichite, (Na, Ca) (Nb, Ti) $[Si_2O_7]2H_2O$ by KUZMENKO and KAZAKOVA (1955). Nenadkevite (U^{4+}, Y, Ce, Th) U^{6+}(Ca, Mg, Pb) $[SiO_4]_2(OH)_4nH_2O$ by POLYKARPOVA (1956). Nickel β-kerolite $(MgNi)_3(OH)_4[Si_4O_{10}]H_2O$ by RUKAVISHNIKOVA (1956), Nickel vermiculite by NIKITINA (1956). Shcherbakovite $Na(K, Ba)_2(Ti, Nb)_2(Si_2O_7)_2$

by ESKOVA and KAZAKOVA (1954). Vinagradovite $Na_5Ti_4AlSiO_{24}.3H_2O$ by SEMENOV, BONSHTEDT-KUPLETSKAYA, MOLEVA and SLUDSKAYA (1956). A new mineral of the type of chinglusuite by DORFMAN (1954). A new mineral of the group of brittle micas by GINZBURG (1955b).

12. *Borates*

Borate minerals are discussed by POVARENNYKH (1956b), SERDYUCHENKO (1956), SHABYNIN and PERTZEV (1956) and SUMIN (1954). The following new borate minerals are described: Alumoferroasharite $(Al, Fe)_2O_3.2B_2O_3.10(Mg, Fe)O{\cdot}6H_2O + 2H_2O$ by SERDYUCHENKO (1956a). Calciborite $Ca_5B_2O_{17}$ by PETROVA (1955). Kurgantaite $(Sr, Ca)_2B_4O_8.H_2O$ by YARZHEMSKY (1952). Preobrazhenskite $3MgO.5B_2O_5.4.5\ H_2O$ by YARZHEMSKY (1956).

13. *Various Minerals*

Tungsten minerals are described by ALBOV (1954), LEVINA (1954), POVARENNYKH (1956b), RIMSKAYA-KORSAKOVA and TROYANOV (1956) and YAKHONTOVA (1954). Columbite-tantalite series of minerals by KUZNETZOV (1956). Fergusonite and euxenite by NEFEDOV (1956b). Titanium minerals by RENGARTEN (1955). Copper minerals by GERSHOIG (1954). Uranium minerals by SOBOLEVA and PUDOVKINA (1956). A large number of non-metalliferous minerals associated with pyritic deposits by LAZARENKO (1954a). Organic minerals: hatchettite by MERLICH and SPITKOVSKAYA (1955); curtisite by MALEEVA (1954), karpathite (carpathite), a new organic mineral, by PIOTROVSKY (1955).

14. *List of New Minerals*

Alumoferroasharite (Borate)
Arsenate-belovite (Arsenate)
Beryllite (Silicate)
Bobkovite (Oxide)
Calciborite (Borate)
Chinglusuite type (Silicate)
Ferrikerolite (Silicate)
Ferroferrimargarite (Silicate)
Ferroselite (Selenide)
Ginzburgite (Silicate)
Hydronasturan (Oxide)
Irinite (Oxide)
Istisuite (Silicate)
Karpathite or Carpathite (Organic)
Karpinskite (Silicate)
Karpinskyite (Silicate)
Kupletskite (Silicate)
Kurgantaite (Borate)
Kurnakite (Oxide)
Kurumsakite (Silicate)
Labuntzovite (Silicate)
Nenadkevichite (Silicate)
Nenadkevite (Silicate)
Nickel β-kerolite (Silicate)
Nickel vermiculite (Silicate)
Phosphate-belovite (Phosphate)
Preobrazhenskite (Borate)
Shcherbakovite (Silicate)
Shorsuite (Sulphate)
Sicklerite group (Phosphate)
Smolyaninovite (Arsenate)
Urhyte (Oxide)
Vinogradovite (Silicate)
Zirconolite (Oxide)

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III. MINERAL DEPOSITS

1. *General*

New books written on the subject of mineral deposits in their various aspects are those by MAGAKYAN (1955a), BILIBIN (1955) and TALDYKINA *et al.* (1954). A detailed scheme of classification of tin deposits is proposed by RADKEVICH (1956b). Biogeochemical methods of prospecting are described by VINOGRADOV (1954) and MALYUGA and MAKAROVA (1956), while the use of indicator minerals in prospecting is outlined by GINZBURG (1954). Various types of mineral associations are discussed by PETROVSKAYA (1955, 1956). Metallogenic zones and provinces are discussed by RADKEVICH (1956a), BELEVTZEV (1954), TUGARINOV (1956); GORZHEVSKY and KOZERENKO (1956b) and GORZHEVSKY *et al.* (1955). Geochemistry of the zone of oxidation of ore deposits is discussed by SHCHERBINA (1955).

2. *Genesis of Ores*

The genesis of various sulphide ores is discussed by BELKOVA *et al.* (1954), BIRYUKOV (1956), GERMANOV (1956); IVANKIN (1954), IVANOV and MITRYAEVA (1956), LAZARENKO (1953), LESNYAK (1954), NEVSKY (1955), OLSHANSKY and RAFALSKY (1956), ROZHKOVA and SHCHERBAK (1957a, b), SHCHERBA (1954), SVESHNIKOV and DOBYCHIN (1956). Various aspects of the problem relating the possible connexion of ore formation with magmatism are discussed by ABDULLAEV (1954), IVANOV and LARYSH (1955), KARASIK (1955), RUB (1956), SMIRNOV (1955) and VAKHROMEEV (1956). Particular associations of tin mineralization with magmatism is discussed by FAVORSKAYA (1955), GRIGORIEV and DOLOMANOVA (1956a), HERZENBERG (1956), BONDARENKO (1956), RUB (1956a, b) and SHIPULIN (1956), while those of tungsten deposits are discussed by GRIGORIEV and DOLOMANOVA (1956a), SHCHEGLOV (1956) and KHRENOV (1955). Various problems relating to different types of ores and their genesis are discussed by ALBOV (1956), EFIMOV (1955), GRECHISHNIKOV (1956), LEBEDEVA (1956), NIKONOVA (1956), PAVLOV and CHUPRYNINA (1955) and RUDNEVA (1956). A general survey of the world's (excluding the U.S.S.R.) uranium deposits, followed by a scheme of genetic classification of these deposits, is provided by MAGAKYAN (1955b).

3. *Sulphide Ores*

Descriptive works on sulphide ores, a number of them incorporating genetic aspects, are those of LAZARENKO (1947), GORZHEVSKY (1955), SALOP (1954), SHCHEGLOV (1956), SHADLUN (1954), and SINDEEVA (1955). Polymetallic sulphide ores of Altai and adjacent regions are discussed by GORZHEVKSY (1956) and GORZHEVSKY and KOZERENKO (1956).

4. *Hydrothermal and Metasomatic Ores*

A classification of skarn ores as based on genetic and metasomatic phases, is attempted by ZHARIKOV (1956). KORZHINSKY (1956a) discusses the processes of metasomatic replacement in the skarn ores. KUROCHKIN (1954) discusses stages of skarn formation, MARCHENKO (1955)—the zonality of skarns. Iron ore skarns are described by LAPIN (1954), POSPELOV (1954) and SUMIN (1954)

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while GORZHEVSKY and KOZERENKO (1952) describe a new type of a magnetite-cassiterite skarn, and SHABYNIN (1955) describes borate skarn minerals.

Other types of hydrothermal and metasomatic deposits are described by DOMAREV (1954, 1956), ITZIKSON (1956), KARASIK (1954), GEORGIEVSKAYA (1955), POLYAKOVA (1956) and RAFIENKO (1956).

A book, edited by KUREK (1954) on altered rocks adjoining ore bodies, contains seven articles dealing with following subjects: skarns by KARPOVA (E.D.) and IVASHENTZEV (A.G.), greisens by NAKOVNIK (N.I.), secondary quartzites by NAKOVNIK (N.I.), sericite-bearing rocks by KUREK (N.N.) and KUREK (A.I.), chlorite-bearing rocks by SHILIN (D.M.) and IVANOVA (V.P.), hydrothermally-altered carbonate rocks by KNYAZEV (I.I.), and, finally, "conclusions" by KUREK (N.N.).

5. *Sedimentary Ores*

GORETZKY (1954) discusses the processes of sedimentary-chemical differentiation as conditioned by differential mobilities of the chemical elements under the influence of variable factors, while SAPOZHNIKOV (1955) discusses the stages of sedimentary ore deposition.

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IV. IGNEOUS AND METAMORPHIC ROCKS

1. *General*

In defining the concepts "rock" and "petrology", KUZNETZOV (1955b) emphasizes the genetic aspects of the true science of rocks, which according to him must strongly link together such concepts as "process", "rock" and "mineral". In another article KUZNETZOV (1955a) suggests that there are essentially three genetic types of igneous rocks, namely granitic type, basaltic type and hyperbasic type. According to him syenites, with which are often associated magmatic iron ores, can be related either to basalts (beta-syenites or to granites (gamma-syenites). The systematics of igneous rocks is revived in a new text book of petrology written by the late prominent Russian petrologist A. N. ZAVARITZKY (1956). There is no lack now in the U.S.S.R. of petrological books and articles translated from the English, as for example a very good translation of the well known book *Theoretical Petrology* by Tom F. W. Barth.

Works on experimental petrology include those of OSTROVSKY (1956) who made experiments on silicate melts containing water, and those of ABRAMYAN (1954), KHITAROV and RENGARTEN (1957), PREOBRAZHENSKY (1955) and VERBITZKY (1954). The extension of the notion of symmetry to structural petrology is attempted by SHAFRANOVSKY (1956).

A book by SOLOVIEV (1952) contains a large amount of statistical information regarding the relative amounts and the average composition of the igneous rocks from eight select provinces of the U.S.S.R. as well by containing valuable discussion of magmatic histories of these provinces during the successive geological periods. The second part of this book contains a detailed account of the Caucasian petrographical province. Caucasian igneous rocks are also discussed by a number of authors, such as AFANASIEV (1954, 1955), BALASANYAN (1956), KADENSKY (1956b) and PAFFENGOLTZ (1954). Problems of magmatism of other parts of the U.S.S.R. are discussed by BORODAEVSKAYA (1956), CHUMAKOV *et al.* (1954), KALYUZHNY (1956), KHAMRABAEV (1956), PINUS (1955) and TOMSON (1956).

2. *Granites*

In a book containing a number of articles on "magmatism and ore deposits" (ZARIDZE *et al.*, 1955), ZARIDZE discusses the origin of the Caucasian intrusive granites, KORZHINSKY, as well as USPENSKY, discuss the problem of granitization, while SUDOVIKOV discusses the relation between granitization and the hydrothermal ore solutions. SHAKOV (1956), while agreeing that the majority of granites are of magmatic origin, contends that the magmas themselves are of metamorphic origin. KOZERENKO and LAZKO (1956) discuss the geological

conditions favouring the formation of granites. GENDLER (1956) discusses the classification of granites, while CHUMAKOV (1954, 1956) discusses the origin and the classification of alkaline granites. Certain granites in northern Russia are described by SHURKIN (1955) and SUDOVIKOV (1954); in Ukraine by LEBEDINSKY and MAKAROV (1956), MATKOVSKY (1956), POLOVINKINA (1954), USENKO (1955) and YURK (1954); in Caucasus by BARANOV and MASURENKO (1955), LESNYAK (1955) and PETROV (1955); in Altai and Kazhakhstan by CHERNOV (1954, 1956), DEMBO (1956) and DMITRIEV (1956); in Siberia by BONDARENKO (1956), BORODAEVSKAYA and SCHMIDT (1956), GRIGORIEV and DOLOMANOVA (1956), GRINBERG (1956), RUB (1956), SHILIN (1956) and SHIPULIN (1956). An important work on a magmatic complex containing rapakivi granite was published by SOBOLEV (1947) who also attempts to explain the origin of this variety of granite.

3. *Pegmatites, Aplites, Greisens and Hydrothermal Veins*

In his detailed classification of pegmatites and of their genetic phases, as well as of the minerals of pegmatites, VLASOV (1955a, b, 1956a, b) comes to the conclusion that granite pegmatites are not formed from the residual fluid of a crystallizing acid magma, but from a magma fraction greatly enriched in volatiles and other low melting point compounds including those of the rare metals. Factors favouring such an enrichment are: the composition of the original magma, the size and shape of the intrusive body, the conditions of cooling, various tectonic factors and finally the crystallochemical factors.

An elaborate discussion of the mineralogy and geochemistry of soda-lithium pegmatites is presented by GINZBURG (1955), the problem of formation of granite pegmatites is discussed by KUZNETZOV (1951, 1954); the problem of zonality of granite pegmatites by BEUS (1954). The paragenic position of spodumene in pegmatites is discussed by KUZNETZOV (1953); that of tourmaline by SLIVKO (1955). Graphic intergrowths of feldspar and quartz are discussed by EVSIKOVA (1955) and the emplacement of pegmatites by GORLOV (1956).

Aplites are discussed by CHESNOKOV (1955) and VLASENKO (1955). Greisens are discussed by DMITRIEVSKY (1956a, b). QUARTZ veins and other types of veins are discussed by LAZKO (1956a, b), LEPCHENKO (1954) and BARABANOV (1954).

4. *Alkaline Rocks*

GERASIMOVSKY (1956) provides a general review of the minerals of the nepheline syenites and discusses the geochemistry and the genesis of agpaitic and miaskitic types of alkaline syenites. Alkaline rocks from various parts of the U.S.S.R. are described by ADAMYAN (1955), ARSENIEV (1954), ARSENIEV and NECHAEVA (1955), BAGADASARYAN (1956a, b), GAPEEVA (1954a, b), POVARENNYKH (1954a), TZAROVSKY (1954) and YASHINA (1955).

5. *Basic and Ultrabasic Rocks*

RAVICH and CHAIKA (1956) give a detailed account of a large layered sheet intrusion some 900 meters thick in the region of the "Siberian Traps" of the Taimyr peninsula in northern Siberia. The intrusive sheet is subdivided into five series, of which the lower ones are composed of banded gabbroidal rocks with a succession of leucocratic and melanocratic bands which the authors

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attribute to the effects of a crystallization differentiation. The uppermost series are made of granitic rocks. The processes of differentiation of magma, giving rise to various igneous rocks occurring in the same region of Siberia, are discussed by DAMINOVA (1956). Various basic rocks in the Vilui basin are described by GONSHAKOVA (1955), LYAKHOVICH (1956a) and SIROTIN (1955). The problem of genesis of the Ukrainian charnockites are discussed by AINBERG (1955), who also introduces a new rock name—kuseevite—for a variety of charnockite. According to USENKO (1956) charnockites from this region were formed through a process of granitization of basic tuffs and tufogenic sedimentary rocks. Various other basic rocks are described by BELOV (1955, 1956), DYMKIN *et al.* (1956), FLORENSKY and LAPINSKAYA (1955), GAPEEVA (1954), KERIMOV (1956), KORZHINSKY and FRANTZKAYA (1955), PASTUSHENKO (1956), PROSKURKO (1955), SOBOLEV (1952) and TKACHUK *et al.* (1955).

SHEINNMANN (1955) describes certain newly discovered pipe-like intrusions of ultrabasic alkali rocks and carbonatites in northern Russia and Siberia. OFFMAN and NOVIKOVA (1955) describe skarn-like rocks infilling a volcanic pipe in Siberia. Other ultrabasic rocks are described by KADENSKY and SERDYUCHENKO (1956), KORZHENEVSKY (1954), MIKHAILOV (1955, 1956), MOSKALEVA (1954), SOBOLEV (1952), VINOGRADSKAYA (1954, 1956), ZAITZEV and LYAKHOVICH (1955).

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6. *Volcanoes and Volcanic Rocks*

A large amount of work has been done on the volcanoes and volcanic products of Kamchatka and Kurile Isles. Descriptions of volcanoes, their activity and their lavas and tuffs are provided by BYLINKINA (1953a, b, c), BYLINKINA and GORSHKOV (1954a, b), BYLINKINA, GORSHKOV and OGORODKOV (1954), KORSUNSKAYA (1956), MARENINA (1956), MARKHININ (1956a), MENYAILOV (1953a, b, c, 1954, 1955), who provided a very extensive memoir on the Shiveluch (Sheveluch) volcano in Kamchatka. NOBOKO (1953a, b, 1954a, b) describes the southermost active volcano in Kamchatka—the Koshelev volcano. Also one should mention the important works of NABOKO and SHAVROVA (1954) and GORSHKOV (1953a, b, c, d, 1954a, b, c, d, 1956). Among other works GORSHKOV gave a detailed account of 83 volcanoes of the Kurile Isles. Also the work of OBRUCHEV and LURIE (154) and those of PIIP (1953a, b, 1954a, b, c, d, 1956a, b) must be mentioned. PIIP is responsible for a large monograph on the most prominent volcano of Kamchatka—the Klyuchevskaya Sopka (1956b). In this work he introduces a new petrographical term "chadalite" which is to replace the French term "enclave" and the English "inclusion". Other works are by PIIP and SVYATLOVSKY (1954), SHAVROVA (1954, 1956), on microelements and radium content in lavas of Kamchatka, SIRIN and TIMERBAEVA (1956a), SVYATLOVSKY (1956a, b, c), TABAKOV (1953a), USTINOVA (1954), VLASOV (1956), VLODAVETZ (1954), and finally by ZAVARITZKY (1954, 1955) who provides a systematic and detailed description of the 71 volcanoes of Kamchatka.

Geysers, solfatara, sublimates and thermal springs are described and discussed by BASHARINA (1953, 1956), GONSOVSKAYA (1956), IVANOV (1956), KVASHA (1954), MARKHININ (1956b), NABOKO (1954c, d, e, f), SIRIN and TIMERBAEVA (1956b), TABAKOV (1953b).

Volcanic rocks from the other parts of the U.S.S.R. are described by BELOV (1956a, b), CHUMAKOV and DIBROV (1956), NECHAEVA (1956), FAVORSKAYA

(1956a, b), FISHKIN (1953), GLADKOVSKY and GUTKIN (1955), GOROSHNIKOV (1956), LAPINSKAYA (1955), LYAKHOVICH (1956b), MKRTCHYAN (1954), NEKHOROSHEV (1955), PORFIRIEV and TKACHUK (1955), RENGARTEN (1955), SOBOLEV *et al.* (1955), TARAKANOVA (1956), TATARINOV (1954), TUZHIKOVA (1956), USENKO and BERNADSKAYA (1954), USTIEV (1956), VLODAVETZ (1955) and VLODAVETZ and SHAVROVA (1953).

7. *Metamorphic and Metasomatic Rocks*

Various metamorphic processes are discussed by BAGDASARYAN (1956), GRUSHKIN (1952), KADENSKY (1956a), KASHKAY and MAMEDOV (1954), KHITAROV (1954), KHODAK (1956a, b), KORZHINSKY (1954, 1956), KOSSOVSKAY and SHUTOV (1956), NALIVKINA (1954), POKROVSKY (1954), POVARENNYKH (1954b), SERDYUCHENKO (1956a, b), SIDORENKO (1952), SUDOVIKOV (1956), VAKHRUSHEV (1956) and ZNAMENSKY (1954).

Metasomatized and contact-metamorphic rocks are discussed by FLORENSKY (1955), KHODUSH (1955), KLAGISH (1956), LAPIN (1954), LOGINOV (1956), MENYALOV *et al.* (1955). Boron minerals and titanium minerals in certain metamorphic rocks are discussed by SERDYUCHENKO (1956) and SHABYNIN (1955); pyroxenes in skarns by ZHARIKOV and PODLESSKY (1955); hydrothermally-altered rocks by BEZPALOV (1956) and VIROVLYANSKY (1954); sodium metasomatism by POLOVINKINA (1955); propylitizes rocks by NOKOVNIK (1954); alteration of minerals by KHODAK (1956), SMIRNOV (1955) and YAKOVLEV *et al.* (1955). Finally VLASENKO (1954) has shown that sandyite, previously described as an igneous rock, is metasomatically altered calcareous xenoliths enclosed in miaskite.

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V. SEDIMENTARY ROCKS

1. *General*

A discussion of the principles of nomenclature, terminology and classification of sedimentary rocks is provided by SHVETZOV (1956), while some new terms are proposed by PREOBRAZHENSKY (1956b). TEODOROVICH (1954, 1956) is discussing in detail the sedimentary geochemical facies and the environmental conditions of the formation of petroleum, iron ores and other formations. GULYAEVA (1955) also discusses the sedimentary facies as related to the oxidation-reduction factor of the environment and to the formation of the organic sedimentary matter.

VINOGRADOV and RONOV (1956b) in their large scale statistical survey of the sedimentary rocks of the Russian platform based on a very large number of samples, covered all the carbonate, argillaceous and arenaceous sedimentary rocks. In volume percentages these three classes of rocks are present in the following amounts: carbonate rocks 47·5, argillaceous rocks 30·0 and arenaceous 19·5. Statistical averages are calculated for the carbonate rocks of various

regions and various ages. Plots of volumes of carbonate rocks and clastic rocks, show a periodicity of deposition of the carbonate rocks with "peaks" situated in the middle or the end of the Caledonian, Hercynian and Tertiary cycles of orogenesis. In another work VINOGRADOV and RONOV (1956a) apply the same statistical methods to the argillaceous rocks of the Russian platform, also based on a large number of samples. Plots of the variation of the chemical composition of the clays against time show such features as the increase of Na and decrease of K with time, the increase of Ca/Mg and SiO_2/Al_2O_3 ratios with time, and other regularities. These features of variation of composition, character of distribution and nature of clays is meticulously discussed in the light of the sedimentology considered from its genetic aspect. Following along similar lines RONOV and KHAIN (1954, 1955, 1956) provide a world survey of sedimentary deposits of the Devonian, the Carboniferous and the Permian periods. SHABAROVA (1955) also discusses the chemical composition of ancient sedimentary deposits.

The minerals of sedimentary rocks and the mineral composition of sedimentary rocks are discussed by PREOBRAZHENSKY and SARKISYAN (1954), PREOBRAZHENSKY (1954a), SARKISYAN (1956), BOBROVNIK (1956), VISTELIUS (1954), ROMANOVA (1954), LOGVINENKO and KARPOVA (1954), VAKHRUSHEV (1954), DISTANOV (1956b), KOBILEV (1956), LAPCHIK (1956), MURAVIEV (1956), KUDRIN (1956), GULYAEVA (1956) and VIKULOVA (1955).

The geochemical characters of sedimentary rocks in their various aspects are discussed by KUDRIN (1956), ARSENIEV and NECHAEVA (1956), KOVDA (1954), SIDORENKO (1956b), BURIANOVA (1954), MIROPOLSKY (1956) and SERDYUCHENKO (1955a).

The geochemical processes and the genesis of sedimentary deposits are discussed by SHCHERBINA (1956), STRAKHOV (1954, 1955, 1956a, b), RUKHIN (1956), KOSSOVSKAYA and SHUTOV (1955), TIMOFEEV (1955), PERELMAN (1954), YANOV (1956), and DANCHEV (1956a, b).

Certain sundry problems are discussed by GINZBURG (1956), DISTANOV (1956a), YURKEVICH (1956), and ABRAMOVICH (1956).

2. *Weathering*

In his book, LUKASHEV (1956) deals with the problems of geochemical zonality as observed in the crust of weathering, especially as it is related to the climatic-vegetation zones of soil types in Russia. The book also provides an excellent summary of the recent Russian work in the field of pedology. PERELMAN (1955a, 1956) discusses the migration capacity of the chemical elements in the crust of weathering; KOVDA (1956) and GERMANOV (1956) the hydrochemical factor of migration; STRAKHOV and ZALMANSON (1955)—the migration and accumulation of iron oxides, and IVANOV the distribution of Li, Rb and Cs in soils.

Specific studies of the ancient crust of weathering in the Urals, Kazakhstan and Central Asia, and other parts of the U.S.S.R. are provided by NIKITIN (1956), RAZUMOVA (1956), PERELMAN (1955b), SHCHUKINA (1956), GINZBURG and VITOVSKAYA (1956), NIKIFOROVA (1956), GINZBURG and RUKAVISHNIKOVA (1956), SIDORENKO (1956a) and ZAVIDONOVA and VESELOVSKAYA (1956).

Various problems of weathering are discussed by GLAZOVSKAYA (1956), KORIN (1956), MIKHAILOV (1954), RIKHTER (1955), SERDYUCHENKO (1954) and YARILOVA (1956).

3. *Clay Minerals*

The kaolinite—halloysite group of minerals is discussed by KUADZHE (1955), ANANIEV and KUKOVSKY (1956) and SLIVKO (1953). A detailed scheme of classification of the minerals of the montmorillonite group is provided by SERDYUCHENKO (1953, 1956), who subdivides them into (a) montmorillonites sensu stricto, (b) beidellites, (c) saponites, and (d) parahalloysites. SERDYUCHENKO (1955b) also discusses the composition and the classification of sepiolites, palygorskites and "attapulgite", the last substance being, according to him, not a pure mineral, but a variety of clay. Palygorskite, talc and pyrophyllite are discussed by DROMASHKO (1953).

Descriptions and discussions of the genesis of various clay minerals are carried out by DZHAVAKHISHVILI (1956), GORBUNOV (1956), GRITZAENKO, BERKHIN and RUDNITZKAYA (1956), PARFENOVA (1956), and SPIRO, GRAMBERG and VOVK (1955a, b).

Clay minerals in sediments are discussed by DZOTZENIDZE *et al.* (1956), LAZAREV *et al.* (1956), PETROV (1954), RATEEV (1956), and SEIDOV (1956).

A comprehensive treatise on the staining method as applied to clay minerals is produced by VEDENEEVA and VIKULOVA (1956). Other works on the staining method are by VEDENEEVA and RATEEV (1955a, b) and SHUKEVICH (1954). The application of electronographic methods are discussed by ZKHUS (1954) and ZVYAGIN (1954, 1956). Finally SEDLETZKY (1954b) shows that a mineral called glinite and another mineral called chasovite do not exist, while LOGVINENKO and FRANK-KAMENETZKY (1955) prove that a mineral called alushtite is really a mixture of dickite and illite.

4. *Clays*

White fireclays and ordinary white clays from the Urals are described in detail by PETROV (1948), who also brings in genetical consideration in the study of these clays and presents a number of instances which support his contention that certain kaolinite clays are derived from mica through the process of weathering. Bentonitic clays from the Ukraine are described by PEKUN (1956), and zinciferous clays from the Kazakhstan by CHUKHRHOV (1956). Other descriptions of clays are by KARYAKIN (1954), KIRSANOV (1955), KIRSANOV and MIROPOLSKAYA (1955), LOGINOVA (1956), NYRKOV (1956), RATEEV (1954), and SAMODUROV (1956).

The genetic aspect of clays is discussed by BUSHINSKY (1956), LOMTADZE (1954, 1955), and MIROSHNIKOV (1956).

Methods of study of clays are discussed by KUADZHE (1954), MIKHAILOV (1955), SPIRO *et al.* (1955b), VEDENEEVA and RATEEV (1955), and VIKULOVA (1956).

The composition and the genesis of loess is discussed by ANANIEV (1955, 1956), KARLOV (1955), LARIONOV (1955), RYABCHENKOV (1954), SEDLETZKY (1954a), SEDLETZKY *et al.* (1954), and VAKHRUSHEV and VAKHRUSHEVA (1954).

The composition and the genesis of bauxites is discussed by BENESLAVSKY (1954a, b, 1956), CHZHI-CHZHEN (1956) and LISITZINA (1956).

5. *Limestones*

A very extensive and novel geochemical-sedimentological study is carried out by RONOV (1956) on the Devonian, Carboniferous and Permian carbonate

rocks of the Russian platform. This study is based on a large number of samples of rocks together with their chemical analyses. The results of this statistical study are presented by numerical tables, variation diagrams and a set of very cleverly coloured and constructed lithological-geochemical maps. It is concluded that such a study provides enough data for the reconstruction of former sedimentogenic environment and consequently leads to the unravelling of the mode of origin of the rocks in question.

Other works dealing with carbonate sedimentary rocks are by BABAEV and AKHRAMKHODZHAEV (1954), BUSHINSKY (1954), FROLOVA (1955), KATCHENKOV (1956), KHOLODOV *et al.* (1956), GROSSHEIM and KOROTKOVA (1956), LOGVINENKO (1956), PALVELEV (1956), VARTANOVA (1954), VESELOVSKAYA (1956), VYALOV (1956), YANATIEVA (1954), and YURK (1956).

Carbonate concretions are described and discussed by DOBROVOLSKY (1955), HAUER (1955), SLIVKO and FISHKIN (1956), TIMOFEEVA (1956), TKACHENKO (1956), and ZARITZKY (1956a, b).

Dolomitic rocks are described and discussed by KHODAK (1956), KHVOROVA (1956), KOLOTUKHINA (1956), KOROLUK (1956), NIKOLAEV (1956) OSIPOVA (1956), SOKOLOV (1955), STRAKHOV (1956c, d), VISHNYAKOV (1956), VITAL *et al.* (1956), YANATIEVA (1955), and ZELENOV (1956).

Methods of study are discussed by PIOTROVSKY (1956) and RUDI (1954).

6. *Phosphates*

BUSHINSKY (1954) in his study of the mineralogy of the phosphate deposits, suggests their classification into five types, as based on the dominant mineral entering into their compositions. These five types are as follows: (1) hydro-apatite, (2) carbonate-apatite, (3) fluor-apatite, (4) francolite, (5) kurskite. SHATSKY (1955a) provides a world-wide survey of phosphorite deposits, which he classifies into three main groups: (1) volcanogenic-siliceous, (2) terrigenic-carbonate, and (3) glauconitic. These are further subdivided into eleven formations.

Phosphate deposits are also discussed by BRODSKAYA and SOLOVIEV (1956), FESENKOVA (1955), FURMAN(1953, 1954), GAVRIKOVA (1956), HIMMELFARB and NARCHEMASHVILI (1955), MALINOVSKY (1955), MASLENNIKOV and KAVITZKAYA (1956), MATZ *et al.* (1956), OREKHOV and SHAMRAY (1956), PETRENK and RENGARTEN (1954), and SHATSKY (1955b).

7. *Silica Deposits*

KALEDA (1956) discusses the genetic types of silica deposits such as the jaspilites, jasperoids and diatomites, which are also discussed by BUSHINSKY and FRANK-KAMENETZKY (1954), LINETZKAYA (1955) and RESHETNYAK (1955). The arenaceous siliceous deposits are described by KANSKY (1955), MANUILOVA (1954), SIDORENKO (1955), and VASILIEV (1956).

8. *Modern sediments*

STRAKHOV (1956a, b) and STRAKHOV *et al.* (1954) discuss the types of sedimentary processes and the formation of sediments. STRAKHOV distinguishes four climatic-environmental sedimentogenic types: (1) glacial, (2) humid, (3) arid and (4) volcanic. SHAMRAY (1956) and KLENOVA (1954) discuss marine sediments, GULYAEVA (1954) discusses the redox potential as a factor in terri-

genous sedimentation and KROTOV (1955) discusses the distribution and the genesis of iron ores and bauxites. Deposits of Bering Sea are studied by LISITZIN (1955a, b, 1956), LIZUNOV and LISITZIN (1955), STARIKOVA (1956a), ZAITZEVA (1954), ZHUZE and SEMINA (1955); those of the Okhotsk Sea by BEZRUKOV (1955a, b), OSTROUMOV (1954, 1955), STARIKOVA (1956b) and ZHUZE (1954); those of the Pacific Ocean by OSTROUMOV and SHILOV (1956a, b), ZAITZEVA (1956); those of the Black Sea, Azov Sea and Caspian Sea and other localities by EGOROVA (1955), GORSHKOVA (1955), PAKHOMOVA (1956), SHABAROVA (1955a, b), SKOPINTZEV and KRYLOVA (1955), BELOV and LAPINA (1956) and KLENOVA *et al.* (1956).

9. *Coals*

Books on coal, its origin and nature, are by GRIGORIEV (1954) and by GAPEEV (1954). A statistical-chemical study of the material balance of the coalification process is attempted by USPENSKY (1954) and his conclusions have an important bearing on the problem of the geochemistry of carbon in the earth's crust. TIMOFEEV (1955a, b, 1956) is discussing the genesis and the classification of coals. ZHEMCHUZHNIKOV (1954, 1955a, b) deals with the problem of accumulation of the coal forming material during successive geological periods, and he also refers to certain aspects of the problem of the genesis of coal. SKOK (1954, 1956) is concerned with the question of the degree of profound metamorphism of coal as related to the volatile content and the specific gravity of coals and anthracites, while KRYLOVA (1954) traces the relation between the degree of metamorphism and the optical properties of coals. Other problems of coal science are discussed by BOGOLYUBOVA (1956), KHODOT and PREMYSLER (1955), KUKHARENKO and SUKHAREV (1954), NIKONOV (1955), RODIONOVA *et al.* (1956) and SHIROKOV (1955).

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10. *Bitumens*

The chemical composition and the nature of hydrocarbons and other organic material found dispersed in sedimentary rocks, are discussed by PETROVA and KARPOVA (1954); PETROVA, KARPOVA and MANDRYKINA (1956), GLADYSHEVA and KOZLOV (1956), RADCHENKO and SAVINYKH (1956) and YURKEVICH (1954). Ozokerite and analogous bituments are described by SNARSKY *et al.* (1955), SOKOLOVA *et al.* (1955), and KHODAK (1955); anthraxolite by STEIBERG (1956); shungite by ALEXANDROV (1956).

The origin of petroleum is discussed by KROPOTKIN (1955), MIRONOV (1954, 1955), MIRONOV *et al.* (1955), PORFIRIEV (1955), RADCHENKO and SHESHINA (1955, 1956), USPENSKY (1955) and WEBER (1955). Other works on petroleum are by BROD (1955), KARTZEV (1954), STRAKHOV *et al.* (1955), TEODOROVICH (1954), WEBER (1956), TAMRASYAN (1954, 1955), VASSOEVICH (1955) and YURKEVICH (1955).

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VI. NATURAL WATERS AND EVAPORATES

In this section only a classified list of author's names and a list of references will be given.

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ADDENDUM

AN important publication has reached me too late to be incorporated in the text of this review. It is a volume entitled *Problems of Geochemistry and Mineralogy*. Publ. Acad. Sci. U.S.S.R., 1956, edited by D. I. SHCHERBAKOV, and dedicated to the memory of ALEXANDER EVGENIEVICH FERSMAN. It contains the following articles:

SHCHERBAKOV (D. I.) The principal features of the creative activity of A. E. FERSMAN, (pp. 5–8).

SAUKOV (A. A.) On the geochemical works of A. E. FERSMAN, (9–18).

SHAFRANOVSKY (I. I.) Mineralogenetic crystallography in the works of A. E. FERSMAN, (19–23).

VOLFKOVICH (S. I.) The ideas of A. E. FERSMAN in the field of chemical technology, (24–36).

KAPUSTINSKY (A. F.) On the theory of the earth, (37–71).

SHCHERBINA (V. V.) The forms of transfer of chemical elements during the processes of mineral formation and conditions of their concentration, (72–82).

VLASOV (K. A.) Emanation process and crystallization differentiation as the leading factors of formation of a series of deposits of rare elements, (83–93).

TUGARINOV (A. I.) On the multi-stage formation of ore deposits, (94–108).

NIKOLAEV (V. A.) On the problem of the theory of processes of endogenic mineral formation, (109–128).

GERASIMOVSKY (V. I.) The tasks of genetic mineralogy, (129–138).

LEMMLEIN (G. G.) The study of formation of liquid inclusions in crystals, (139–141).

SHEFTAL (N. N.) The genesis of the piezo-quartz deposits in its relation to the data concerning the artificial growth of quartz, (142–157).

CHUKHROV (F. V.) and ERMILOVA (L. P.) New data on kerchenites, (158–157).

Note: The articles by KAPUSTINSKY and SHCHERBINA are discussed in Part I.

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THE ELECTRICAL PROPERTIES OF THE EARTH'S INTERIOR

D. C. TOZER

INTRODUCTION

THIS article attempts to describe our present knowledge of the electrical properties of the mantle and core of the earth. In keeping with other fields of geophysics, we shall assume that the properties of the earth are functions of the radial distance only, except perhaps for local variations of at most a few kilometres extent. These may be neglected in examining the broad picture of the earth's interior. Some direct evidence for the hypothesis of spherical symmetry will be described below, but its success in seismology gives added support to its use in the present connexion.

The discussion of the electrical properties of the mantle, which forms the larger part of this article, is divided into a number of sections. Section I describes the methods by which observations of the geomagnetic field at the earth's surface enable one to form some idea of the electrical conductivity of the earth's interior and also the results, using these methods, of various workers.

In Section II the experimental work on the conductivity of minerals that might be of importance in a discussion of the earth's mantle is reviewed and an interpretation of these data is given.

Section III describes how the experimental data may be combined with its theoretical interpretation to give an explanation of the conductivity distribution in the mantle. In particular, a model that assumes that magnesium-rich olivines are a major constituent of the mantle is discussed. Comment is made on the validity of such a model and the temperature distribution required to fit the conductivity distribution.

In Section IV the effect of the electrical conductivity on the thermal properties of the mantle is discussed and an attempt is made to evaluate the thermoelectric and Hall effects in the lower mantle.

Section V is a brief discussion of the electrical properties of the core.

SECTION I

Observations of the geomagnetic field at any place on the earth's surface reveal that it is subject to a variety of temporal variations of both a periodic and aperiodic nature. Of the periodic variations, a series of extended observations reveals that the diurnal variation, whose phase depends on local apparent solar time, has the largest amplitude. There is also an approximately diurnal periodic variation produced by the moon, whose amplitude varies considerably throughout the lunar month. Many other periodic variations have been found which correspond to various astronomical cycles, but these data have not yet been utilized in finding the electrical conductivity of the mantle. These periodic

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variations do not, in general, show any appreciable dependence on longitude, but they do vary considerably with latitude. There are comparable changes produced in all three components (north, east and vertical) of the magnetic field.

The aperiodic variations of the field, which are associated with sunspot activity, may be much larger in magnitude than the diurnal variation. The most marked change in the field in latitudes between 60° N and S is in the northward component. When the normal periodic variations, which are enhanced during a magnetic storm, are subtracted from the observed field values, a characteristic behaviour is found. In both northern and southern hemispheres there is, at first, an increase in the northerly component that commences almost simultaneously all over the earth. After a few hours, this trend is reversed and the intensity falls below the average value by a larger

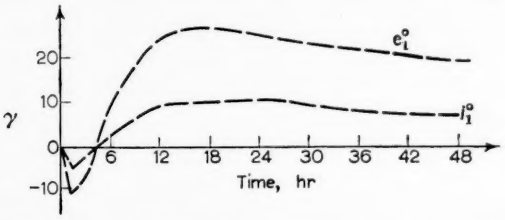

Fig. 1. The time variation, during the first two days of a magnetic storm of the coefficients e_1° and i_1° of the main spherical harmonic components (P_1°) of the disturbance field; e_1° refers to the part of external origin; i_1° to the part of internal origin (after CHAPMAN and WHITEHEAD, 1923) ($1\gamma = 10^{-5}$ gauss).

amount than the initial positive increment. This decays to its pre-storm value over a period of some days (Fig. 1). The sense of the changes in the vertical component in low latitudes is different in the northern and southern hemispheres but in high latitudes the variations are more complex (see CHAPMAN and BARTELS, Vol. 1).

It is well known that in the absence of electric currents flowing through the earth's surface, it is possible to analyse the magnetic field at the surface into parts of external and internal origin (CHAPMAN and BARTELS, Vol. 2). This type of analysis of the periodic variations of the field was first made by SCHUSTER and has been repeated by CHAPMAN (1919) and others (BENKOVA, 1940; HASEGAWA, 1943). Unlike the steady geomagnetic field which is more than 95 per cent (possibly entirely) of internal origin, the periodic and the magnetic storm-time variations have external components that are somewhat larger than the internal contribution.

It is convenient to represent the potential V of the magnetic field in a series of spherical harmonic functions $P_n^m(\cos\theta)\cos(m\phi + \delta)$ from which the field, $\mathbf{H}$ may be derived by the relation:

$$\mathbf{H} = -\operatorname{grad} V$$

When the assumption is made that the periodic variations do not depend on longitude, one may represent the potential of the disturbance field by the expression:

$$V = C + \sum_{n=1}^{\infty} \sum_{m=0}^{n} \left(e_n^m \frac{r^n}{R^{n-1}} \cos(mt + \varepsilon_n^m) + i_n^m \frac{R^{n+2}}{r^{n+1}} \cos(mt + i_n^m) \right) P_n^m(\cos\theta)$$

where C is a constant, t the time, and R is the radius of the earth. The first and second terms in the brackets represent the potential of the externally and internally generated magnetic fields. The results of harmonic analysis are conveniently expressed by the ratio of the amplitudes e_n^m/i_n^m and the phase differences $\varepsilon_n^m - i_n^m$ of the same harmonic in the external and internal potential. The results obtained by CHAPMAN (1919) and others are shown in Table 1. The amplitude of the

Table 1(a). Solar Diurnal Variation

Harmonics P_{m+1}^m

	Amplitude ratios $\left(\frac{e_{m+1}^m}{i_{m+1}^m}\right)$				Phase differences $(\epsilon_{m+1}^m - i_{m+1}^m)$			
m	Mean 1905	Equinox 1902	Mean 1905	Solstice 1902	Mean 1905	Equinox 1902	Mean 1905	Solstice 1902
1	2·9	2·7	2·8	3·0	− 5°	− 23°	− 3°	− 20°
2	2·4	2·0	2·3	2·2	− 18°	− 17°	− 19°	− 18°
3	2·4	2·5	2·7	2·4	− 21°	− 21°	− 20°	− 21°
4	2·2	2·9	2·3	3·2	− 23°	− 30°	− 15°	− 24°
1	2·30*		2·34†		− 9°*		− 5°†	
2	2·43*		2·30†		− 10°*		− 5°†	
3	2·25*				− 14°*			

Unmarked data after Chapman. * After Hasegawa. † After Benkova.

Table 1(b). Lunar Diurnal Variation

(after CHAPMAN)

Harmonics P_{m+1}^m

	Amplitude ratios $\left(\frac{e_{m+1}^m}{i_{m+1}^m}\right)$			Phase differences $(\epsilon_{m+1}^m - i_{m+1}^m)$		
m	Mean	Equinox	Solstice	Mean	Equinox	Solstice
1	1·9		2·8	− 29°		− 23°
2	1·5		1·8	− 29°		− 29°
3	2·7		2·7	− 14°		− 19°
4	2·0		2·7	− 17°		− 52°

principal harmonic P_1^c in the external and internal field of the aperiodic variation is plotted as a function of time in Fig. 1.

Harmonic analyses of the periodic variation have been made by several workers, and this gives an indication of the uncertainties present in the analyses. The north or east components may be used in turn with the vertical components to determine the amplitude and phase relationships of the harmonics. The results generally differ by significant amounts. It has been suggested that these differences represent a non-potential field due to electric currents flowing from the air to earth or the occurrence of harmonic terms with a longitude dependence. However, SCHMIDT (1918) showed that the non-potential field was too small to explain the discrepancies. Although it is now known that there is an appreciable dependence of the diurnal variation on longitude in the neighbourhood of the equator, it is generally believed that the discrepancies chiefly arise from the approximate nature of the representation of the field by a small number of harmonic terms. Comparison of the results of different workers indicates a 10 per cent uncertainty in the amplitude ratios and about 8° in the phase difference.

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It will be noticed in Table 1 that the amplitude ratios and phase differences for corresponding harmonics of the lunar and solar variation are the same when allowance is made for uncertainties, especially in the small lunar effect. The magnitude of the diurnal variations changes considerably during the year and the sunspot cycle, but the relationship of the external and internal harmonics is maintained. These observations strongly suggest that the internal and external effects do not have independent causes but that the smaller internal field is induced by the external magnetic field.

It may be shown mathematically that there is no unique solution of the problem of finding the electric current distribution in the earth that produces a given magnetic field at the earth's surface and from this result it is not difficult to see that any attempt to find the electrical conductivity in the earth from the induced magnetic fields at the surface has a similar uncertainty. For this reason, it is necessary to use models of the earth's interior in studies of the induction effects and to discover the best of the models of a given type. If we assume that the whole of the periodic field of internal origin is induced by the external field, we may compare the results of harmonic analysis with those calculated using a particular model of the earth's interior. It is possible that both magnetic and electromagnetic induction are present, but it is difficult to separate the two effects by observations of the magnetic field at the earth's surface. The good, even perfect agreement of the calculated results with the field observations does not imply that one has found the actual conductivity or magnetic permeability distribution within the earth. This fact has been overlooked by some workers in the field and unless explicitly stated, it leads to misunderstanding by other geophysicists. Of course, one may possess independent data which enables one to reject many of these "perfect" models or favour some rather than others, but this essential uncertainty should not be forgotten.

The type of model is specified by the form of the expression used to represent the distributions of electrical conductivity σ and magnetic permeability μ in the earth. The arbitrary constants appearing in these expressions are adjusted to give the best agreement of the calculated induced magnetic field with observations. Let us consider the model of the earth that has been most frequently

used (CHAPMAN and PRICE, 1930, RIKITAKE, 1950), i.e. a core of constant permeability and conductivity surrounded by an insulating ($\sigma = 0$), non-magnetic ($\mu = 1$) shell. Then it may be shown that for the daily variations the phase relationships of the external and internal harmonics are determined to a very good approximation by the ratio $\frac{\sigma}{\mu}$. It is possible that in a different model the dependence on the individual values of σ and μ might be sufficient to allow some estimate of them to be made, but it is to be expected, bearing in mind the arbitrary nature of models, that such values are likely to be most uncertain. To distinguish between magnetic and electro-magnetic induction and hence determine σ and μ separately from the magnetic field observations, the obvious method is to examine slowly varying magnetic fields at the earth's surface. As the rate of change of the inducing field decreases, the magnetic effects eventually predominate over the electromagnetic effects. The difficulty here is to find large, slowly varying inducing fields. (Fields with a period of several days are required.) CHAPMAN and PRICE (1930) have attempted to find the effects of magnetic induction in the slow decay of the field after a magnetic storm, but the fields were too small to obtain any positive indications of magnetic induction.

Fortunately, we may utilize laboratory data to give almost certain evidence that the magnetic permeability of the earth is very close to unity below a depth of a few tens of kilometres. Those comparatively few materials for which the permeability may differ appreciably from unity, have a characteristic temperature known as the Curie point, above which they lose their abnormal magnetic properties and μ becomes nearly one. The Curie point for the different magnetic materials ranges up to temperatures of the order of 700°C, which is exceeded at small depths. Furthermore, the variation of this quantity with pressure is quite minute ($\sim 10^{-5}$°C/bar—PATRICK, 1954), so that we may be sure that no known magnetic material could be magnetic below a few tens of kilometres. We shall therefore assume $\mu = 1$ in the following discussion.

The periodic variations of the field are, to a first approximation, independent of longitude and symmetrical about the equator. This is additional evidence that the electrical conductivity of the mantle is a function of the radius only, and makes the mathematical analysis of induction very much simpler. It may be shown as a consequence of this symmetry that any harmonic of the inducing field only gives rise to the same harmonic in the induced field. A description will now be given of the efforts of CHAPMAN and his co-workers to elucidate the conductivity distribution in the earth. This work has been selected for special consideration because it has led to a distribution of conductivity that is easier to reconcile with other data on the interior of the earth and the electrical properties of minerals than some distributions suggested by other workers.

The earliest models to be considered were of the conducting "core" type (see above) in which the radius and conductivity of a uniform core was found from the amplitude ratios and phase differences of the principal harmonics in the daily variations (CHAPMAN and PRICE, 1930). The phase difference of each harmonic was sufficient to find a value of the conductivity σ_c (assuming $\mu = 1$) for the core and this value of σ_c was used in conjunction with the amplitude ratio for a given harmonic to determine the radius of the core. It was possible to obtain good agreement with all the observational data on the daily variations (phase differences and amplitude ratios for harmonics P_2^1, P_3^2, P_4^3, P_5^4) with a core of

conductivity 3·6, $10^{-4}\ \Omega^{-1}\text{cm}^{-1}$ and a radius 0·96 the radius of the earth. This corresponds to a non-conducting outer layer 250 km thick. It may be noticed that this value of the electrical conductivity of the core is about one hundred times greater than that for a typical dry rock and about a hundred times less than sea-water.

It is obvious that the actual situation in the earth is not well represented by such a model as that described above since we know that the conductivity of the surface layers, especially the oceans, is sufficiently high to make the idea of an insulating shell unrealistic. This has led to a number of studies which attempt to evaluate the effects of the currents induced in the oceans. Due to the great differences of conductivity between land and sea the current systems induced in the oceans will be grossly affected by the surrounding land. The first attempt to solve this problem (CHAPMAN and WHITEHEAD, 1923) made no attempt to discuss the effects of the boundaries, but replaced the oceans and the moist conducting layers at the surface of the earth by a spherical conducting shell. This is a very rough approximation since even ten miles of moist earth is only equivalent to 125 ft of sea-water in its effect on the induced fields. To evaluate the effects of the surface layers, a given amplitude ratio and phase difference was taken for the P_2^1 and P_3^2 harmonics and the depth and conductivity of the core were calculated (see Table 2). It was shown that if the equivalent ocean depth exceeded about half a mile, the phase difference of the P_3^2 harmonic below the surface shell became positive, which was incompatible with any core model of the conductivity distribution. RIKITAKE (1950) has attempted to make a more realistic estimate of the oceanic effect by studying the effects of currents induced in an ocean of various depths bounded by meridians 90° apart. He has found that near the boundaries of the ocean the effects are greatest in mid-latitudes where the electric currents flowing in an ocean 1000 m deep may give a horizontal intensity of one or two γ ($1\gamma = 10^{-5}$ gauss). This is of the order 30 per cent or so of the internally generated magnetic field.

The effect of the ocean on the induction in the mantle is most important for harmonics with the shortest period. The situation is analogous with "skin

Table 2. The Effect of the Oceans on the Calculations of the Depth and Conductivity of a Conducting Core (after CHAPMAN *and* WHITEHEAD*)*

Depth of Ocean*	P_2^1		P_3^2	
	σ_c ($\Omega^{-1}\,\text{cm}^{-1}$)	d_c (miles)	σ_c ($\Omega^{-1}\,\text{cm}^{-1}$)	d_c
125 ft.	$3{\cdot}55 \cdot 10^{-4}$	168	$5{\cdot}7 \cdot 10^{-4}$	191
250 ft.	$3{\cdot}5 \cdot 10^{-4}$	178	$6{\cdot}9 \cdot 10^{-4}$	210
1320 ft.	$4{\cdot}7 \cdot 10^{-4}$	198	$13{\cdot}9 \cdot 10^{-4}$	336
2640 ft.	$10{\cdot}4 \cdot 10^{-4}$	340	—	—

* Conductivity of oceans $4{\cdot}10^{-2}\ \Omega^{-1}\,\text{cm}^{-1}$

effect" phenomena observed in high frequency circuits in the laboratory. The electric currents induced by an oscillating magnetic field at the surface of a conductor may be considered, to a first approximation, to occur only to a depth which is proportional to $1/\sqrt{\sigma\nu}$ where ν is the frequency and σ the conductivity. The more slowly varying magnetic fields of the aperiodic disturbances will therefore induce currents at greater depths and be less affected by the conductivity of superficial layers than the daily variations.

If the conductivity distribution found from the daily variations and described above is extended to a discussion of the currents induced in the mantle by a magnetic storm, large discrepancies with the observations are found. To obtain a good fit with the data, the conductivity of the core must be increased by a factor of ten, or even more if the core is smaller. It is not easy to determine the radius of the core from the storm-time variations.

The impossibility of obtaining agreement with all the data, using the simple conducting core model, indicates that the model is inadequate. A solution of the problem may be obtained if the surface layers are sufficiently conducting to shield the layers at greater depths from the periodic variations but at the same time, sufficiently insulating to have a small effect on the storm-time variation. It is usual to consider the oceans and moist sedimentary layers of the continents as the shielding layer and this idea has enabled agreement to be obtained with all observations.

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The extension of the mathematics to the more physically plausible case of induction in a spherically symmetrical earth but with conductivity varying as a power of the radius, was made by LAHIRI and PRICE (1938). They considered models of the earth in which the conductivity was given by:

$$\sigma = k\left(\frac{qR}{r}\right)^s \qquad r < qR \qquad s > 0 \qquad 0 < q < 1$$

$$\sigma = 0 \qquad r > qR$$

This type of distribution reduces to the "core" model already discussed if $s = 0$ and $q < 1$. They first investigated the range of s values which would enable good agreement to be found with the data for the internally induced P_3^2 harmonic of the solar diurnal field, which is the one most accurately known. If a particular s value is chosen, the amplitude ratios and phase differences determine q and k. It was found that if s was increased, q had to be increased and k decreased to obtain a good fit. An upper limit of about 30 to the range of s values was fixed by the maximum value of unity for q. k was then equal to $4{\cdot}10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (distribution "c", Fig. 2). When these distributions were used to find the induced field during a magnetic storm the agreement was found to improve with increasing s, but with $s = 30$ the agreement was not perfect. At this stage, the conducting surface layer was introduced which enabled s to be increased to give good agreement with all the data. A surface conducting layer of thickness d and conductivity σ_s was considered and it was found that for a given s there was a range of values of $\sigma_s d$ compatible with the storm-time and P_3^2 harmonic data of the daily variation. The upper limit of $\sigma_s d$ was independent of s and equal to $5{\cdot}1\ .\ 10^3\ \Omega^{-1}$. With this value of $\sigma_s d$ the distribution of conductivity in the mantle was of the "core" type, the radius being 0·903 R and with a conductivity of at least $10^{-2}\ \Omega^{-1}\ \mathrm{cm.}^{-1}$ (distribution "e", Fig. 2). The actual value of

conductivity, if greater than this, makes negligible difference to the calculated induced magnetic field. The least value of $\sigma_s d$ which enabled a good fit to be made with all the data was $2 \cdot 10^3\ \Omega^{-1}$ with corresponding values of $q = 1$, $s = 37$ and $k = 4 \cdot 10^{-5}\ \Omega^{-1}\,\text{cm}^{-1}$ (distribution "*d*", Fig. 2). Although it is not possible to distinguish between distributions lying between "*d*" and "*e*", of Fig. 2 with the P_3^2 harmonic of the daily variations and the storm data, other harmonics of the daily variation indicate that distribution "*d*" is a better fit than "*e*".

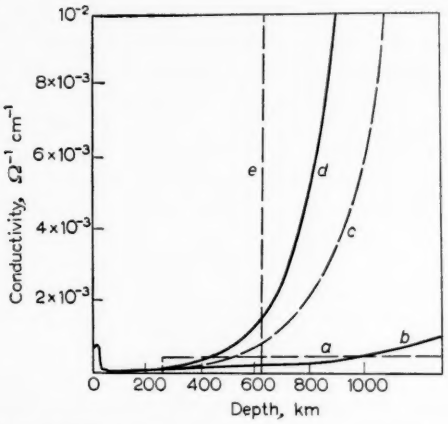

Fig. 2. Conductivity distribution in the upper mantle compatible with the data of Table 1; only distributions between "*d*" and "*e*" are also compatible with the storm-time observations.

More recent analyses of the daily variations by BENKOVA (1940) and HASEGAWA (1943) have been used by RIKITAKE (1950) to find the conductivity distribution in the mantle. In confining his attention to the core model of the conductivity distribution he found that deeper but more conducting cores were required by the smaller phase differences of the P_3^2 harmonic in the newer data.

It is not known in detail what would be the values of q, k, s calculated with this data and the LAHIRI and PRICE model, but rough calculation indicates that the k values would be lower and the s values greater than those required to fit CHAPMAN's data.

If the contributions to the surface magnetic field of the induced currents in various ranges of the depth are calculated for LAHIRI and PRICE's model, it is found that there is no appreciable effect from currents in layers below about 1000 km unless the period is greater than a few days. Information on the conductivity of the earth below this depth has been obtained by other methods, in particular the secular variation of the geomagnetic field.

Observations of the geomagnetic field over periods of the order of years reveal that the secular variation is mainly confined to about a dozen regions of perhaps a few thousand kilometres in extent. The behaviour in each centre appears to be independent of that elsewhere. It may be shown that this secular variation field is of internal origin and that it probably arises near the boundary of the mantle and liquid core. The pattern of secular variation changes

profoundly in a time of the order of one hundred years and for this reason it is usual to attribute its origin to processes in the liquid core. A distribution of varying magnetic dipoles, such as would arise with electromagnetic induction in eddies in the surface layers of the core, can give a good representation of the secular variation (LOWES and RUNCORN, 1951). The field observations also reveal a general drift of the centres of secular variation to the west (BULLARD *et al.*, 1950).

The first estimates of the electrical conductivity of the lower mantle were made by BULLARD (1950) using his theory of the westward drift of the secular variation field and some experimental data of COSTER (1948). He demonstrated that the effect of electromagnetic torques between the mantle and core, which may be shown to be the most important way in which the core and mantle are coupled, is to give the intermediate depths of the core approximately the angular velocity of the mantle (the core must differentially rotate to conserve angular momentum if there is radial convection). If the secular variation has its origin in fluid motions at the surface of the core, the coupling will make the centres of secular variation drift westward, the lines of force being fixed in the fluid. The coupling is between meridional electric currents flowing in the mantle, produced by the differential rotation of the core in the dipole field, and the dipole field in the mantle. He found that a conductivity of at least $0{\cdot}1\ \Omega^{-1}\ \mathrm{cm}^{-1}$ was required in the lower mantle to give the observed westward drift.

The random fluctuations in the length of the day have also been utilized to find the conductivity of the lower mantle. If it is assumed that these fluctuations in the rate of rotation of the mantle are due to a readjustment in the division of angular momentum between the core and mantle, the value of the electromagnetic couple required to produce the angular acceleration may be calculated. A conductivity of the order $1\ \Omega^{-1}\ \mathrm{cm}^{-1}$ is required. The chief uncertainty in these calculations is the value of the toroidal magnetic field near the core-mantle boundary.

RUNCORN (1955) has used data on the spectrum of the secular changes in declination to find the mean conductivity of the mantle. By examining the records of the older magnetic observatories and the data on the magnetization of varved clays, HUGHES and MOORE (unpublished) were able to plot the amplitude of the declination changes against their period. Assuming the mantle to be uniformly conducting, the attenuation of the secular variation by the mantle could be calculated for various values of the mean conductivity. The unattenuated spectrum was compared with what might be expected on theoretical grounds. A mean value of between 1 and $10\ \Omega^{-1}\ \mathrm{cm}^{-1}$ was derived for the conductivity of the lower half of the mantle.

A more sophisticated calculation of the conductivity in the lower mantle has been made by MCDONALD (1957), who calculated the attenuation by the mantle of a random distribution of secular variation sources at the core boundary. He found a value of about $2\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for the conductivity at the core boundary. He has given a diagram of the conductivity distribution throughout the mantle (Fig. 3). This curve is in substantial agreement with all the calculations of the mantle conductivity that have been made. In the upper mantle he chose a distribution intermediate between LAHIRI and PRICE's "*d*" and "*e*" distributions (Fig. 2) and it seems likely that this will be in agreement with the more modern

field analyses of the daily variation by HASEGAWA and BENKOVA. In Section III we shall try to interpret MCDONALD's conductivity distribution in the light of our knowledge of the conductivity processes in minerals and the physical conditions in the mantle.

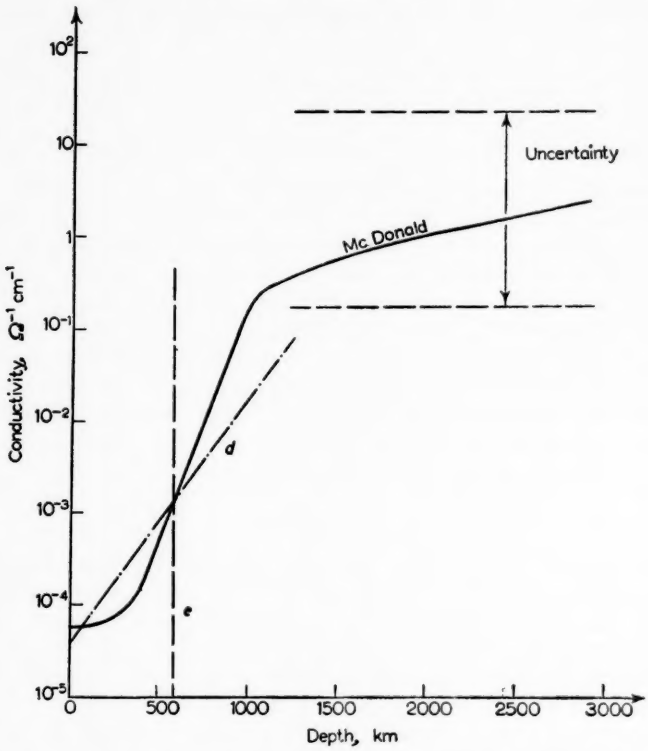

Fig. 3. Conductivity distribution of McDonald for the whole mantle, with Lahiri and Price's "*d*" and "*e*" distributions for comparison.

SECTION II

In the past decade, there have been several measurements of the electrical conductivity of minerals which are likely to occur in the mantle. The experimental work of HUGHES (1953) will be briefly described because of its scope and range of experimental conditions.

The most important variable governing the conductivity of minerals is temperature. Plots of the logarithm of the conductivity against the reciprocal of the absolute temperature T, indicate a dependence of the type:

$$\sigma = \sum_r \sigma_r e^{-\frac{A_r}{T}}$$

where σ_r and A_r are constants. For some materials, there are three values of r but for others, melting of the solid limits the number to two. Due to the very

different values of the σ_r's and A_r's, and the exponential nature of the dependence, one may make a good approximation to the total conductivity at most temperatures by only one term.

Let us consider the general nature of the conductivity processes that occur in the ultrabasic minerals, each of which are represented by one term in the above expression. At the lowest temperatures, the conductivity may be expressed by:

$$\sigma_{\text{imp}} = \sigma' e^{-\frac{E'}{2k_0 T}}$$

where we have replaced A_r by $\frac{E'}{2k_0}$. k_0 is Boltzmann's constant. The characteristic energy E' of this process is in the range $0{\cdot}5 - 1{\cdot}0$ eV for the most commonly occurring members of the olivine series [$(Mg,Fe)_2 SiO_4$], ($\sim 90\%$ Mg_2SiO_4) and ortho-pyroxene series [$(Mg,Fe)SiO_3$]($\sim 90\%$ $MgSiO_3$); σ' lies between 10^{-4} and 10^{-6} Ω^{-1} cm^{-1}. It is believed that this process is an impurity conductivity and probably the effect of the iron ions in the lattice. This is not an important conductivity mechanism in the mantle, since the maximum impurity conductivity σ' occurring in typical minerals is much less than the conductivity in the mantle calculated from the magnetic observations.

The impurity conductivity mechanism is usually swamped by an intrinsic electronic conductivity process as the temperature is raised beyond 900°–1000°K. If the conductivity for this process is represented by:

$$\sigma_{\text{int}} = \sigma_1 e^{-\frac{E_1}{2k_0 T}}$$

E_1 is $\sim 3{\cdot}0$ eV and $\sigma_1 \sim 1 - 5$ Ω^{-1} cm^{-1} for the magnesium-rich olivines. For enstatite and diopside the E_1 values are $\sim 2{\cdot}0$ eV and $\sigma_1 \sim 0{\cdot}1$ Ω^{-1} cm^{-1}. It is believed that the conductivity in this temperature range of minerals of the olivine and ortho-pyroxene series containing more than about 85 per cent of the magnesium end member, is independent of the exact composition of the mineral but characteristic of the respective magnesium end member.

At temperatures greater than 1400°–1500°K the conductivity of the mineral is mainly ionic. If the equation representing this is:

$$\sigma_{\text{ion}} = \sigma_2 e^{-\frac{E_2}{k_0 T}}$$

we have $E_2 \sim 3{\cdot}0$ eV and $\sigma_2 \sim 5{\cdot}10^6$ Ω^{-1} cm^{-1} for the magnesium-rich olivines; for enstatite $E_2 \sim 2{\cdot}8$ eV and $\sigma_2 \sim 10^4$ Ω^{-1} cm^{-1}; for diopside $E_2 \sim 4{\cdot}0$e V and $\sigma_2 \sim 10^{10}$ Ω^{-1} cm^{-1}. These figures are subject to greater uncertainty than those for the other conductivity mechanisms because of the difficulties of making measurements at high temperatures and the limited temperature range in which the observations can be made. The ionic nature of the conductivity process may be inferred from polarization experiments.

It has already been mentioned that the conductivity distribution in the mantle cannot be explained as an effect of impurity conduction, and we shall therefore confine the theoretical discussion to the intrinsic semiconduction and ionic conductivity processes. The energy E_1 characteristic of electronic intrinsic semiconduction may be interpreted as the width of the energy gap at absolute zero between the highest filled valence bands and the lowest empty conduction band of the electronic band structure. The energy gap changes with temperature and

pressure, its variations being conveniently measured by examination of the displacement of the ultraviolet absorption edge. This absorption is due to optical excitation of electrons to the conduction band and changes in the position of the long wavelength edge of the absorption band can give an indication of changes in E_1. If the temperature dependence is linear, which is a good approximation, the temperature coefficient of E_1 appears in the expression for σ_1, the intercept of the curve $\log \sigma_{\text{int}} - 1/T$ on the σ axis. The expansion of the lattice, and changes in the electron-lattice vibration interactions both contribute to the temperature dependence of E_1. The former may be calculated from the effect of pressure on E_1 and appears to be small in comparison with the effects of lattice vibration. The latter interaction may be divided into the effects of acoustical and optical modes of lattice vibration. Calculation indicates that the polarization effects created by the optical modes are much more important in changing E_1 than the dilations characteristic of the acoustical modes. This is in agreement with observations on other semiconductors with considerable ionic bonding.

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The effect of pressure is to diminish the value of E_1 for olivine, this being the only mineral which has been studied in any detail. The theory of this effect is poorly understood and no theoretical expression can be given. It is usual to assume that the percentage change in E_1 is proportional to the percentage change in volume (MOTT and GURNEY, 1948). This is in general agreement with the idea that E_1 will tend to zero with sufficiently large compression, i.e. the material would eventually acquire metallic properties. $\left(\frac{\partial E_1}{\partial P}\right)_T$ has been measured for an olivine (RUNCORN, 1956).

The expression for σ_1 in semiconductors which have a sufficiently small free electron concentration for Boltzmann statistics to be used is:

$$\sigma_1 = 2\left(\frac{2\pi k_0 T}{h^2}\right)^{\frac{3}{2}} m_e^{\frac{3}{2}} m_p^{\frac{3}{2}} e(\mu_e + \mu_p) e^{-\frac{1}{2k}\left(\frac{\partial E_1}{\partial T}\right)_p}$$

where h is Planck's constant, m_e and m_p the effective masses of electrons and holes, μ_e and μ_p the mobilities of electrons and holes, and e their charge. We are interested in relative changes of σ_1 in the mantle and have to consider the effects of pressure and temperature on the various quantities in this equation. It has already been stated that $\left(\frac{\partial E_1}{\partial T}\right)_p$ is primarily due to the interaction of electrons with optical modes of lattice vibration and we may use an approximate theoretical expression for this quantity derived by RADKOWSKY (1948). From this, $\left(\frac{\partial E_1}{\partial T}\right)_p$ is expected to decrease with increasing pressure and in the lower mantle is about a third of its value at zero pressure. The exponential dependence of σ_1 on this factor makes this effect of considerable importance in estimating the conductivity in the lower mantle where this is more dependent on the value of σ_1 than E_1 (see Section III, p. 428). The effective masses m_e, m_p may be assumed to remain constant to a good approximation so that μ_e and μ_p are the only other variables.

A discussion of the variation of mobility with pressure and temperature cannot be made with any confidence until experimental measurements of this quantity have been made. There are indications from photo-conductivity

experiments that the mobility of the electrons is much lower than might be expected from any scattering effect of the lattice or its imperfections. This might be expected physically from the fact that the metallic ions are well separated and do not appreciably overlap, especially when iron replaces several per cent of the magnesium ions. This lack of overlap with adjacent identical ions would make the electronic bands derived from the levels of the metallic ions narrow. In these circumstances, the normal theory of electronic conduction in bands might be inappropriate, the process of electron transfer being better visualized as a series of jumps over potential barriers. This is similar to ionic conductivity and leads to low values of the drift mobility. In the absence of any direct measurements of mobility, two models of the electron transfer process have been considered. In one, the mobility is determined by the scattering of electrons by the optical modes of lattice vibration, which may be shown to be the most important of the normal scattering mechanisms. In the other, the mobility is determined by the alternate trapping and excitation process described above. The two models give rather similar results for the variation of σ_1 throughout the mantle. The lattice scattering model indicates that σ_1 remains constant to about a factor of two throughout the mantle and the other model gives an increase by about a factor of three if the temperature is $\sim$ 5000°K at the core boundary. σ_1 is roughly constant with the second model if the temperature is $\sim$ 3000°K near the core. Both these calculations ignore the effect of phase transitions in the mantle, which might change σ_1 by a greater amount.

The effects of pressure and temperature on the ionic conductivity process are rather easier to evaluate. The pressure coefficient $\left(\frac{\partial E_2}{\partial P}\right)_T$ for a magnesium-rich olivine has been measured by HUGHES (1955), who finds an increase of $4{\cdot}8\ 10^{-6}$ eV/bar. This increase may be interpreted in the following way: the expression for E_2 involves the height of the potential barriers separating adjacent defect sites and the energy of formation of a lattice defect. Compression of the lattice by the application of pressure will make it more difficult (increase the potential barriers) for the ions to pass through the lattice. MOTT and GURNEY (1948) suggest that the percentage changes in E_2 are proportional to the percentage changes in volume, and so the above pressure coefficient may be used with compressibility data to find the value of E_2 as a function of density. This calculation indicates that E_2 may be as large as 8·0 eV in the lower mantle. The temperature dependence of E_2 is included in the expression for σ_2 when the value of σ_2 is derived from experimental plots of $\log \sigma_{\text{ion}} - 1/T$. It may be attributed to the expansion of the lattice as the temperature is raised.

The effects of temperature and pressure on σ_2 are small. Calculation shows less than a 50 per cent variation throughout the mantle.

To study the conductivity distribution in the mantle, it is necessary to know if the conductivity is predominantly due to electrons or ions. This is conveniently discussed by calculating the temperature T_c at which the intrinsic semiconduction and ionic conduction are equal. The temperature T_c is given by:

$$T_c = \frac{E_2 - \frac{E_1}{2}}{k_0 \log_e \frac{\sigma_2}{\sigma_1}}$$

To determine the value of T_c and the conductivities at a given depth, the various quantities in the equations should be taken at constant volume. This modification increases the experimentally determined value (at constant pressure) of σ_1 for the magnesium-rich olivines by a factor of two and decreases the value of σ_2 by a factor of five. The calculations* of T_c and the various conductivity parameters are shown in Table 3 and T_c is plotted throughout the mantle in Fig. 4.

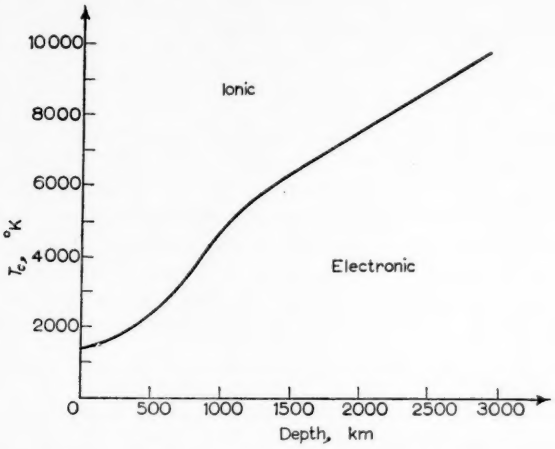

Fig. 4. The temperature (T_c) at which the ionic conductivity equals the electronic conductivity for a mantle mainly consisting of magnesium-rich olivine.

Table 3. Parameters Governing Intrinsic Semi-conduction and Ionic Conduction in a Mantle Composed of a Magnesium-rich Olivine ($\sim 90\%$ Mg_2SiO_4)

Depth (km)	$[\sigma_1]_v$ (Ω^{-1} cm^{-1})	E_1 (eV)	$[\sigma_2]_v$ (Ω^{-1} cm^{-1})	E_2 (eV)	T_c(°K)
0	5	3·2	1·0 . 10^6	3·00	1450
200	7	3·14	0·9 . 10^6	3·24	1680
400	6	2·94	0·9 . 10^6	3·55	2100
600	7	2·85	0·8 . 10^6	3·87	2650
1000	8	2·43	0·7 . 10^6	5·55	4900
1400	11	2·34	0·7 . 10^6	6·15	6100
2200	16	2·18	0·7 . 10^6	7·08	8000
2900	15	2·08	0·7 . 10^6	8·0	9800

* All the quantitative results given hereafter are for a mantle of magnesium-rich olivine ($\sim$ 90 per cent Mg_2SiO_4).

Comparison of the value of T_e with modern estimates of the temperature distribution in the mantle (see the article of VERHOOGEN in VOLUME 1 of this series) shows that below a few hundred kilometres T_e is greater than the estimated temperatures.* A predominantly olivine mantle may therefore be considered to be an electronic semiconductor below a few hundred kilometres. At shallower depths the contribution of ionic conductivity has to be considered. The increase in T_e with depth is to be expected for the other minerals that might occur in the mantle, since the increase is mainly determined by the rise in E_2, which is readily understood physically (see above).

SECTION III

The conductivity distribution may be used to calculate the temperature distribution in the mantle if certain assumptions are made regarding the composition and the disposition of phases forming the mantle material. If the texture of the material is a single phase containing inclusions of foreign material, then the bulk conductivity is determined almost entirely by the conductivity of the continuous phase. For example, if perfectly conducting inclusions occur as a random distribution of spheres occupying a third of the volume, the bulk conductivity is only 2·5 times the conductivity of the continuous phase. In the upper mantle where the exponent $\frac{E_1}{2k_0T}$ is large and the dependence on temperature is strong, the error introduced into the temperature calculations by the presence of other phases distributed as above only amounts to a few tens of degrees for quite large "impurity" contents.

The precision of temperature determination from the electrical conductivity is highest in the upper mantle where the conductivity has a strong dependence on temperature. In the lower mantle, where the conductivity calculated from magnetic field observations is comparable with the value of σ_1, the conductivity is slowly dependent on temperature, and the uncertainties of the conductivity data make the temperature uncertain by hundreds of degrees. In this region, estimation may best be given in the form of a lower limit to the temperature. However, the weak dependence of the conductivity on temperature in the lower mantle also means that errors in the calculation of E_1 at these depths are not as important as in the upper mantle.

This is important in view of the possible occurrence of high pressure phases in this region. For example, it has been demonstrated by RINGWOOD (1957 and private communication) that spinel-structured modifications of the iron-rich members of the olivine series exist at high pressures and it is reasonable to expect similar behaviour for the magnesium-rich members. The co-ordination of the metallic ions is the same in both structures and one would not expect a large change in E_1 that could not be explained by the difference in density of the two phases. σ_1 is not likely to change by a large factor during the phase transition.

It is reasonably certain that the material forming the mantle has more than one component, so that any phase transition is likely to be spread over a range of depth. If we imagine a spinel-olivine phase transition taking place for an olivine having an appreciable amount of both end members, then there will be

* It is also greater than the temperature calculated from the conductivity distribution see below).

a considerable range of temperatures and pressures in which the spinel and olivine phases of different composition coexist. The conductivity in such a two-phase region will be largely determined by the continuous phase. The geological evidence suggests a considerable contraction of the earth over the past 10^9 years which could be explained by the phase transition proceeding in the sense olivine → spinel since the latter has the higher density. Little can be said at present about the way in which the spinel-structured crystals would occur in the olivine phase, but for reasonably small concentrations of the spinel form, the bulk conductivity would probably be determined by the olivine phase.

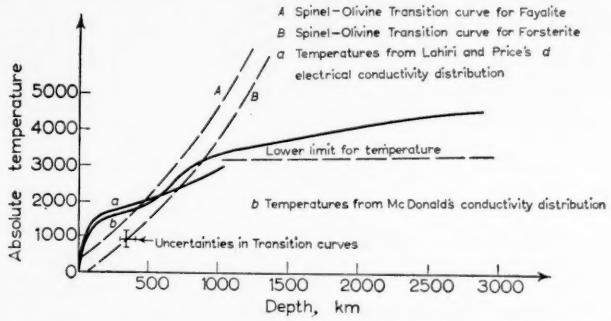

Fig. 5. Temperatures derived from conductivity distribution; olivine–spinel equilibrium curves.

If the conductivity distributions of LAHIRI and PRICE for the upper mantle and MCDONALD for the whole mantle are used to find the temperature distribution in a mantle composed mainly of olivine (~ 10 per cent fayalite), the curves in Fig. 5 are obtained. The temperature in the transition region (~ 400–900 km depth) was obtained by drawing a smooth curve through the temperatures calculated at 400 and 600 km, assuming olivine determines the conductivity, and at 1000 km, assuming spinel to be the only phase present. Incidentally, the continuous nature of the phase transitions suggests that the first order discontinuities in the "e" conductivity distribution of LAHIRI and PRICE (Fig. 2) and RIKITAKE (1950) are incorrect. The density of the olivine phase at 600 km, from which the value of E_1 is calculated, was obtained by extrapolating BULLEN's density distribution between the base of the crust and 400 km depth. It will be seen that an increase in the temperature gradient occurs as the depth increases beyond 400 km and that the calculated temperature curve lies between the phase equilibria curves (dotted) for the olivine end members found by RINGWOOD (private communication).

An increase in the temperature gradient at such great depths has not been considered in detail before and it seems appropriate to suggest some possible explanations of the phenomenon. The most acceptable explanations of the increased temperature gradient are based on the occurrence of a phase transition in this region. Since the predominant mode of heat transfer in the mantle is not known with certainty three cases will be considered. They are:

1. Convection throughout the whole mantle.
2. Convection only in the region above the transition zone.
3. Conduction only in the whole mantle.

1. It is generally recognized that for convection to occur in the mantle the actual temperature gradient has to exceed the adiabatic gradient (see VERHOOGEN Vol. 1 of this series). The amount by which the adiabatic gradient should be exceeded to give convection currents of sufficient velocity to account for the heat flow and mountain building processes, depends on the plastic and elastic properties of the mantle material. We have hardly any quantitative knowledge of these properties in the earth except a few calculations of "viscosity" from the damping of the changes in latitude and the rise in the earth's surface that occurs when the load of an ice-cap is removed. If the mantle behaves as a Newtonian fluid with this "viscosity" ($10^{20} - 10^{22}$ poises), then it may be shown that the excess temperature gradient is small when compared with the adiabatic gradient. With this assumption, a calculation of the adiabatic gradient can lead to a knowledge of the temperature at all depths given the temperature at one depth.

The adiabatic gradient is given by:

$$\left(\frac{\partial T}{\partial r}\right)_s = \frac{\alpha g T}{C_p}$$

where α is the coefficient of expansion, g the acceleration of gravity and C_p the specific heat at constant pressure. The effects of a phase transition have not been considered in the calculations of the adiabatic gradient in the mantle, and it will be demonstrated below that this leads to considerable changes in the calculations for the transition region. The phase change is accompanied by the evolution or absorption of latent heat L which RINGWOOD calculates as about 100 cal/gm, and a change in volume ΔV. The complete phase change may be induced by heating or cooling at constant pressure through a temperature range ΔT, say. We may define an effective specific heat $C_p' = L/\Delta T$ and coefficient of expansion in the phase transition region $\alpha' = \dfrac{\Delta V}{V \Delta T}$. ΔT has not been measured but values of the order a few hundred degrees or less would be expected for the different members of the olivine series. If we take $\Delta T = 300°\text{C}$, $\dfrac{\Delta V}{V} \sim 0{\cdot}1$ (RINGWOOD, 1958) we find α' about fifty times the coefficient of expansion for a single phase and C_p' about twice the value for a single phase. These figures give 3°C/km for the adiabatic gradient in the transition region, which is about ten times that usually quoted for the rest of the mantle. (As $\Delta T \to 0$, the adiabatic gradient tends to the phase transition gradient, $\sim 4°\text{C/km}$.) The increase in temperature gradient and the width of the transition zone, ~ 500 km, is therefore understandable.

2. If convection occurs only in the upper mantle, we may treat this region as one of higher thermal conductivity than the transition zone and lower mantle. With a continuous heat flow in the mantle there will be some steepening of the temperature gradient in the transition zone which will tend to the gradient of the phase equilibrium curves as the effective heat conductivity in the upper mantle increases.

3. If conduction is the only important method of heat transfer in the mantle, the temperature may be obtained by solving the conduction equation:

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho C_p} \nabla^2 T + A$$

where κ is the thermal conductivity, ρ the density and A the heat production per unit volume. In the two phase region the thermal conductivity will be mainly determined, like the electrical conductivity, by the continuous phase (KERNER, 1956). Even if the spinel phase thermal conductivity is considerably greater than that of the olivine phase, the thermal conductivity will be approximately that of the olivine phase until the spinel fraction becomes of the order of 40 per cent or more. On the other hand, the effective specific heat is about three times greater than that for the single phases. From the above equation it may be seen that an increase in C_p is equivalent in its effect on the solution of the conduction equation to a decrease in the thermal conductivity. One has to remember that the heat flow decreases with increasing depth in the earth but it seems reasonable to believe that the variation in $\frac{\kappa}{\rho C_p}$ would be fast enough to give an increase in the temperature gradient in the transition region.

In view of the generality of the above arguments, one might say that if a phase transition is accepted as the explanation of the considerable changes in elastic properties that occur at depths between 400 and 900 km, then an increase in the temperature gradient is likely.

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In the upper mantle the temperatures calculated from the conductivity distribution tend to be rather lower than those given by other methods. (See VERHOOGEN, p. 39 Vol. 1 of this series.) The gradient between 200 and 400 km is about 1°C/km which is also rather lower than usually found. This low gradient may be purely the effect of the type of model of conductivity distribution used. If the uncertainty in conductivity in this region is a factor of two, the uncertainty in temperature, using the olivine model, is about 100°C.

It may be noticed that the steep rise in conductivity around 700 km cannot be

Table 4. Temperatures T_σ Calculated from Conductivity Distributions of MCDONALD (McD) *and* LAHIRI *and* PRICE (L.P.) *with ratios of Ionic to Electronic Conductivities*

Depth	$[T_\sigma]_{McD}$ (°K)	$\left[\frac{\sigma_{ionic}}{\sigma_{elect}}\right]_{McD}$	$[T_\sigma]_{L.P.}$ (°K)	$\left[\frac{\sigma_{ionic}}{\sigma_{elect}}\right]_{L.P.}$
200	1580	0·4	$\leqslant$ 1670	$\leqslant$ 0·95
400	1730	0·07	$\leqslant$ 1880	$<$ 0·25
600	2220	10^{-2}	2220	10^{-2}
1000	3300	10^{-3}	—	—
1400	3600	$8{\cdot}10^{-4}$	—	—
1800	3800	$6{\cdot}10^{-4}$	—	—
2200	4000	$2{\cdot}10^{-4}$	—	—
2900	4500	10^{-4}	—	—

used as evidence for or against compositional changes in the mantle at this depth. It has been seen that this behaviour can be expected for a pure substance with the appropriate parameters, σ_1 and E_1 and a smoothly increasing temperature with depth.

A lower limit of about 3300°K for the temperatures below 1000 km can be estimated for an olivine mantle. An upper limit of about 5000°K at 1000 km and 9000°K at the core boundary is fixed by the great increase in the ionic conductivity at these temperatures. A temperature of 4500°K is suggested for the core boundary, with an uncertainty of several hundred degrees. The relative constancy of the conductivity below about 1500 km at about 1–10 Ω^{-1} cm^{-1} is also an indication that intrinsic semiconduction determines the conductivity at these depths, assuming the temperature increase in this range of depth to be at least several hundred degrees.

If the modified adiabatic gradient in the transition region is taken into account, the large scatter of the temperature estimates at the core boundary is reduced. The difficulty of reconciling a liquid iron-nickel core with the old adiabatically determined temperatures is removed and all the modern estimates of temperature at the bottom of the mantle are in the neighbourhood of 4000°K.

SECTION IV

It may be shown by quite general arguments that the free electrons responsible for the electrical conductivity of the mantle will also contribute to its thermal conductivity. The free electron density in the lower mantle is sufficiently small for classical statistics to be applicable and in these circumstances the electrical conductivity σ is related to the electronic thermal conductivity κ by the equation:

$$\kappa = A\sigma T \left(\frac{k_0}{e}\right)^2$$

where e is the electronic charge and A is a constant. This equation is of the same form as the Wiedemann–Franz relation for which $A = \pi^2/3$. A depends on the nature of the electron scattering process but is always of the order 3. (BLATT, 1957). If $T = 4000$°K and $\sigma < 10\ \Omega^{-1}$ cm^{-1} we find $\kappa < 10^{-4}$ cal/cm sec °C. This is quite negligible when compared with the likely value of thermal conductivity due to lattice vibrations and radiation in the lower mantle.

The exact evaluation of the Hall effect in the lower mantle requires a knowledge of the mobility of both electrons and "holes" and the conductivity. However, a maximum value of the Hall coefficient R defined by:

$$E_H = R\vec{j} \wedge \vec{H}$$

(E_H the Hall voltage, j the current density and H the magnetic field) may be found from the conductivity and an estimate of the order of the mean mobility (μ_M) of the charge carriers. It may be shown that:

$$R_{\max} = \frac{B\mu_M}{\sigma}$$

where B is a dimensionless coefficient of the order unity whose exact value is determined by the type of scattering (FAN, 1955, LEWIS and SONDHEIMER, 1955).

If one assumes that the mobility of the carriers is determined by their scattering by optical modes of lattice vibration (see above), an approximate formula (SCANLON and PETRITZ, 1955) gives $\mu_M \sim 10$ cm^2/V sec. If the conductivity is $\sim 10\,\Omega^{-1}$ cm^{-1}, we find:

$$R_{max} \sim 1 \text{ cm}^3/\text{coulomb}$$

This is comparable with the value assumed by VESTINE (1954) in his Hall theory of geomagnetism.

It may be shown that in the presence of a Hall effect the lines of current flow are rotated through a small angle, the Hall angle, which is of the order $\mu_M H$. For the magnetic fields to be expected in the lower mantle this angle is only 10^{-7} radians. The rotation of the lines of current flow through this small angle increases the resistance of the current paths and this precludes regeneration by the Hall effect to produce the main geomagnetic field in the manner suggested by VESTINE (1954).

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The thermoelectric properties of the lower mantle are interesting in that they may have some relevance to the problem of the origin of the geomagnetic field. The most favoured site for the production of thermoelectric voltages is the core-mantle boundary because of the large change in physical properties across it and its great extent. The thermoelectric properties of semiconductors are often much larger than those of metals and we may ignore the thermoelectric properties of the core in finding to a first approximation the e.m.f. at the boundary.

The absolute thermoelectric power Q of a semiconductor is given by (JOHNSON and LARK-HOROVITZ, 1953, HOWARTH and SONDHEIMER, 1953).

$$Q = -\frac{k_0}{e}\frac{(C-1)}{(C+1)}\left[\frac{E_1(P,T)}{2k_0T} + D\right]$$

where $E_1(P,T)$ is the value of E_1 at pressure P and temperature T, C is the ratio of electron to hole mobility and D is a constant. The constant D depends on a number of factors but is usually of the order of 2 or 3. We may obtain a maximum value for Q by putting $\frac{C-1}{C+1} = 1$, its maximum value. Putting $E_1(P,T) \sim 1$ eV, $T \sim 4000°$K we find $Q_{max} \sim 300\,\mu$V/°C. This is rather smaller than usually assumed (RUNCORN, 1954).

It has been shown (RUNCORN, 1954) that if the earth is spherically symmetrical, voltages on the core-mantle boundary cannot generate the magnetic field observed at the earth's surface. However, the field set up by thermoelectric currents might provide the small initial magnetic field necessary for a dynamo theory of the origin of the geomagnetic field (BULLARD, 1954).

SECTION V

The electrical conductivity of the core cannot be estimated very precisely from geophysical observations at the earth's surface. RIKITAKE (1952) attempted to find the electrical conductivity from the damping of seismic disturbances in the core and the absence of any evidence of the conversion of seismic waves into magneto-hydrodynamic waves. He was only able to say that the conductivity was in the range $10^{12} - 10\,\Omega^{-1}$ cm^{-1}. A much better way of estimating the

conductivity is to examine the theoretical expressions and experimental data on the conductivity of metals, assuming the core is composed mostly of iron. ELSASSER (1946) expressed the electrical conductivity of iron by the equation:

$$\sigma = \frac{C\theta^2}{T}$$

where θ is the Debye temperature, T the absolute temperature. He treated C as a constant, although the more precise expression (BLATT, 1957, p. 297) indicates that it may vary approximately as the cube of the density. This would increase ELSASSER's estimates by a factor of about two. On the other hand, ELSASSER made no allowance for the increase in resistance on melting. The data on the increase in resistance on melting for other materials suggest an increase by a factor of two which cancels out the factor introduced above and leaves ELSASSER's estimate of $1{\cdot}3.\ 10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for the conductivity of a liquid iron core unchanged.

BULLARD (1948, 1950) estimated the conductivity of iron in the core by extrapolation of laboratory data. He allowed a factor of two increase for the effect of pressure, which is as good an estimate as can be made with BRIDGEMAN's (1952) data. He finally adopted a figure of $3.10^3\ \Omega^{-1}\mathrm{cm}^{-1}$ for the conductivity of a liquid iron core at 10,000°K, but regarded this as probably rather low. (BULLARD, 1954). These figures should be increased by two if the temperature is of the order 5000°K.

The largest uncertainty in estimates of the core conductivity is the effect of alloying, for it seems quite possible that nickel and sulphur are present in the core material. BRIDGEMAN (1952) has measured the pressure coefficient of resistance of a series of iron-nickel alloys. The first addition of nickel decreases the conductivity and reduces the positive pressure coefficient of conductivity, but at larger concentrations the coefficient becomes large and negative. For these reasons one expects the conductivity of the core material to be less than $10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and probably greater than $10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$ if the percentage of non-ferrous material is not more than a few per cent.

CONCLUSION

The methods by which knowledge of the electrical properties of the mantle and core have been obtained are described. The arbitrary nature of conductivity distributions found from the geomagnetic field variations is mentioned and, in particular, reasons are given for suspecting that first order discontinuities in the conductivity distribution do not occur.

It is shown that although the ultrabasic minerals exhibit both electronic semiconduction and ionic conduction at atmospheric pressure, the mantle below a few hundred kilometres may be treated as an electronic semiconductor. At shallower depths in the mantle the ionic conductivity is comparable with the electronic conductivity.

A derivation of the temperature distribution from the conductivity distribution is given, assuming the mantle is composed mainly of a magnesium-rich olivine ($\sim$ 90 per cent Mg_2,Sio_4). This shows a steepening of the temperature gradient in the transition region between depths of 400 and 900 km. A number

of explanations of this are given which are based on different models of the heat transfer process in the mantle. It is also shown that the rapid rise in conductivity in the neighbourhood of 700 km cannot be interpreted as evidence for or against a compositional change. A temperature of 4500°K which is uncertain by several hundred degrees is suggested for the core-mantle boundary. The Hall coefficient and thermoelectric power are estimated in the lower mantle. A maximum value of 300 μV/°C is suggested for the thermoelectric power of an olivine mantle, which is rather lower than previous estimates.

The various methods of estimating the conductivity of the core are described and attention is drawn to the considerable uncertainty due to materials dissolved in the iron. A value between 10^3 and 10^4 Ω^{-1} cm^{-1} is most probable.

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